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Materials Balance for Anilines
Level I - Preliminary

JRB Associates Inc.
McLean, VA

Prepared for

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9 May 80

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Materials Balance for Anilines

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This report presents a Level I materials balance study of a group of anilines specified in a Task Order from the Office of Toxic Substances, U.S. Environmental Protection Agency. The compounds studied were aniline, aniline hydrochloride, aniline hydrobromide, o-, m-, and p-nitroanilines, 16 other nitroanilines, and 15 other chloro- and bromoanilines. Areas of major interest were production quantities, producers, consumption quantities, and emissions to air, land, and water related to these processes. The estimated amounts of 1978 production (where available) were as follows: aniline, 279,000 kkg; aniline hydrochloride, 4.6 - 100 kkg; o-nitroaniline, 3641 kkg; m-nitroaniline, 0 - 2.3 kkg; p-nitroaniline, 13,000 kkg. Emissions were estimated when direct data were unavailable. The results (in kkg/year) were: aniline, 20 kkg to air, 0.08 - 5.6 kkg to water; p-nitroaniline, 0.13 kkg to air, 117 kkg to water. Throughout the report, estimates and assumptions were made where justified, in lieu of direct data. Types of information required for future studies are noted.

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ANILINES

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Task No. 10
Contract No. 68-01-5793
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Submitted: May 9, 1980

ABSTRACT

This report presents a Phase I materials balance study of a group of anilines specified in a Task Order from the Office of Toxic Substances, U.S. Environmental Protection Agency. The compounds studied were aniline, aniline hydrochloride, aniline hydrobromide, *o*-, *m*, and *p*-nitroanilines, 16 other nitroanilines, and 15 other chloro- and bromoanilines. Areas of major interest were production quantities, producers, consumption quantities, and emissions to air, land, and water related to these processes. The estimated amounts of 1978 production (where available) were as follows: aniline, 279,000 kkg; aniline hydrochloride, 4.6 - 100 kkg; *o*-nitroaniline, 3641 kkg; *m*-nitroaniline, 0 - 2.3 kkg; *p*-nitroaniline, 13,000 kkg. Emissions were estimated when direct data were unavailable. The results (in kkg/year) were: aniline, 20 kkg to air, 0.08 - 5.6 kkg to water; aniline hydrochloride, 0 kkg to air, 4.6 - 100 x 10^{-3} kkg to water; *p*-nitroaniline, 0.13 kkg to air, 117 kkg to water. Throughout the report, estimates and assumptions were made where justified, in lieu of direct data. Types of information required for future studies are noted.

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EXECUTIVE SUMMARY

This Phase I materials balance reports on emissions due to production and use of several representatives of the class of anilines. The compounds designated by the Task Order for study were the three isomeric nitroanilines, aniline hydrochloride, aniline hydrobromide, and a list of 38 other nitro-, chloro-, and bromoanilines, plus the parent compound, aniline. Of these compounds, no information was available on three (2,4,6-tribromoaniline hydrobromide, 2-bromo-4,6-dichloroaniline, and 4-bromo-3,5-dichloroaniline).

The anilines studied were characterized as being solids at room temperature with very low water solubilities and relatively low vapor pressures. The exceptions to this generalization were aniline itself (a water-soluble liquid), o- and m-chloroaniline (liquids), and all aniline salts (very water-soluble).

Aniline

Aniline is synthesized industrially by vapor-phase hydrogenation of nitrobenzene. An estimated 279,000 kkg were produced in 1978. Generated emissions due to direct production were estimated to be 20 kkg to air and 0.08 - 5.6 kkg to water. Aniline was consumed by the following six categories of uses in 1978: isocyanate synthesis (148,000 kkg; 50% of total consumption), rubber chemicals (80,000 kkg; 27%), dyes and intermediates (17,800 kkg; 6%), hydroquinone (14,800 kkg; 5%), drugs (8,900 kkg; 3%), and miscellaneous uses (herbicides, fibers totalling 27,000 kkg; 9%). In addition a small amount of aniline hydrochloride was synthesized from aniline. Between 47% and 60% of aniline production was used captively, mostly for isocyanate synthesis. Imports and exports each contributed less than 1% to aniline availability and use, respectively. Generated emissions due to aniline consumption (by category of use) were estimated to be: isocyanate synthesis, 19 kkg to air, 3,700 kkg to water; rubber chemicals, 20 kkg to air, 3,900 kkg to water; dyes and intermediates, 4 kkg to air, 900 kkg to water; hydroquinone, 4 kkg to air, 700 kkg to water; drugs, 0 kkg to air, 85 kkg to water; and miscellaneous, 3 kkg to air, 680 kkg to water.

These data are shown on the aniline materials balance, included here as Figure ES-1.

Aniline Hydrochloride

Aniline hydrochloride is the salt formed by neutralizing aniline base with HCl. Direct production data were not available from USITC or from the producers themselves, so production was estimated on the basis of deductions and impressions gained from industrial sources to be 4.6 - 100 kkg/yr. Generated emissions due to production were estimated to be ~ 0 kkg to air and $4.6 - 100 \times 10^{-3}$ kkg to water. Imports and exports made very small contributions to production and consumption totals. Aniline hydrochloride was stated by an industry source to be used almost exclusively in the dye industry. Based on information from these personal communications, emissions to water during dye production were estimated to be in the range $2.3 - 77 \times 10^{-2}$ kkg aniline hydrochloride per year. Figure ES-2 is the materials balance for aniline hydrochloride.

Aniline Hydrobromide

Although it was judged that aniline hydrobromide was synthesized from aniline in a manner analogous to aniline hydrochloride, no information was available on production or consumption of aniline hydrobromide.

o-Nitroaniline

o-Nitroaniline is synthesized by the ammonolysis of o-chloronitrobenzene. A reported 3,641 kkg/year were produced in 1978. Generated emissions due to this production were estimated to be 69 kkg to water. It was not possible to estimate air emissions. *o*-Nitroaniline has two major industrial uses; synthesis of *o*-phenylenediamine and synthesis of dyes. No quantitative data were available so estimates of generated emissions from those consumption processes were not possible.

Figure ES-3 displays the available information about *o*-nitroaniline.

m-Nitroaniline

m-Nitroaniline is synthesized by the partial reduction of *m*-dinitrobenzene. No production data were available, indicating the smaller industrial role played by *m*-nitroaniline relative to the *ortho* and *para* isomers. A rough estimate placed production in the range 0 - 2.3 kkg/yr. in 1978. 47 kkg were reported as imports in 1978. Major uses for m-nitroaniline were as an intermediate in the synthesis of dyes, as photographic anti-fogging agents, and in coccidiostatics, interior paint pigments, and synthetic sweeteners. Quantitative consumption and use data were also unavailable. Lack of data in these areas precluded estimation of reasonable emissions due to production and consumption processes. Refer to Figure ES-4 for the materials balance of m-nitroaniline.

p-Nitroaniline

p-Nitroaniline is synthesized by the ammonolysis of p-chloronitrobenzene. It is quantitatively the most important of the three nitroaniline isomers, with an estimated production in 1978 of 13,000 kkg. Generated emissions due to production were estimated to be 0.13 kkg to air and 117 kkg to water. p-Nitroaniline was used chiefly in the rubber chemicals industry (6,000 kkg; 40% of total consumption). Other uses were dyes and intermediates (20%), gasoline additives (20%), pharmaceuticals and veterinary (7%), agricultural chemicals (3%), and miscellaneous (10%). The % contributions were 1969 values. Generated emissions due to these uses were estimated to total 68 kkg to air and 600 kkg to water in 1978. These data are summarized on the materials balance for p-nitroaniline, Figure ES-5.

Other Nitroanilines

The other anilines containing a nitro group (with or without other ring substituents) were considered as a group. No quantitative data were available on either production or use. Therefore, emissions could not be estimated. In general, these compounds were used predominantly by the dye industry.

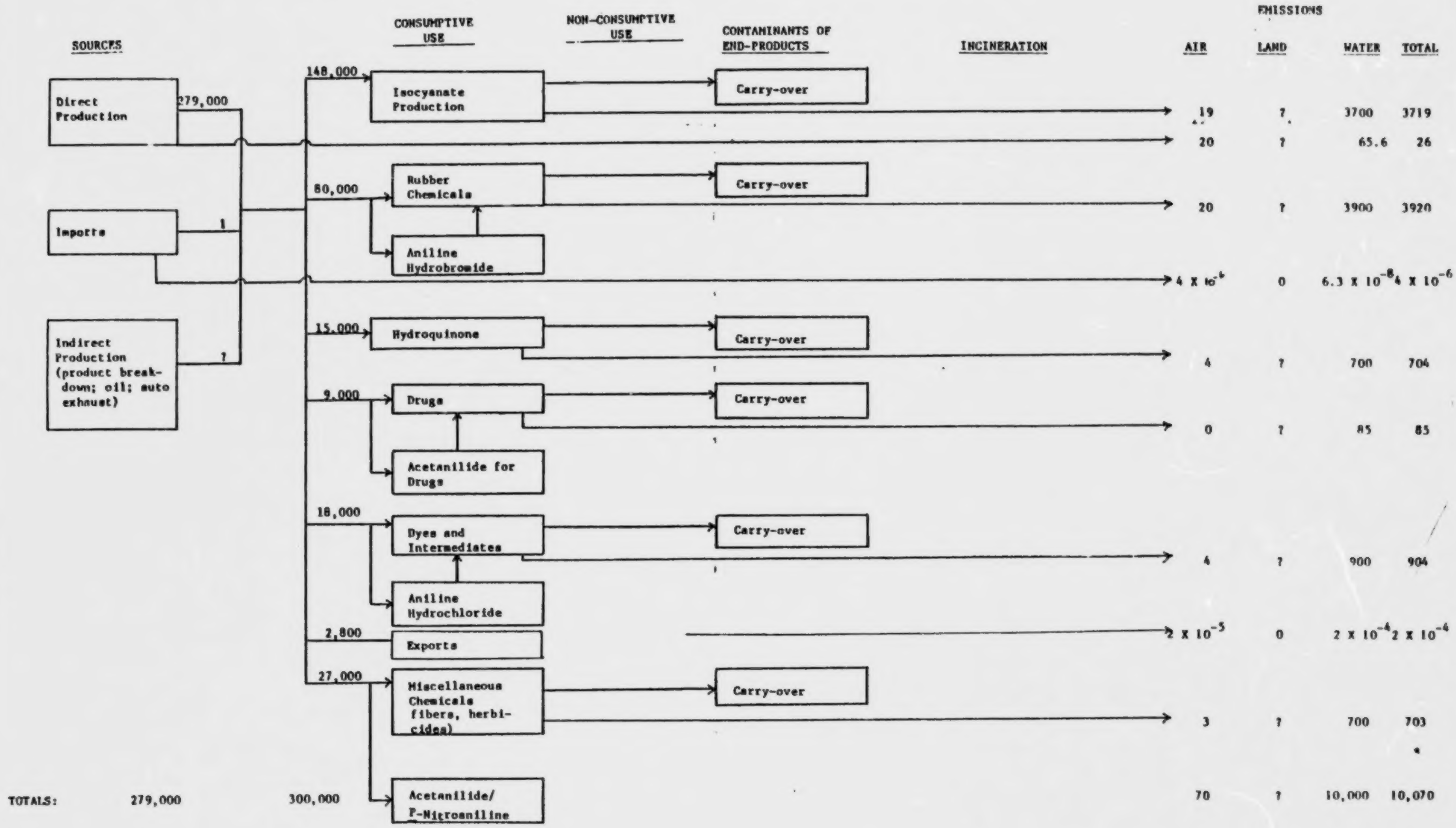
Chloro- and Bromoanilines

As with nitroanilines, the halogenated anilines were considered as a group. No quantitative data were available, so emissions could not be estimated. These compounds seem to be used primarily by the dye industry.

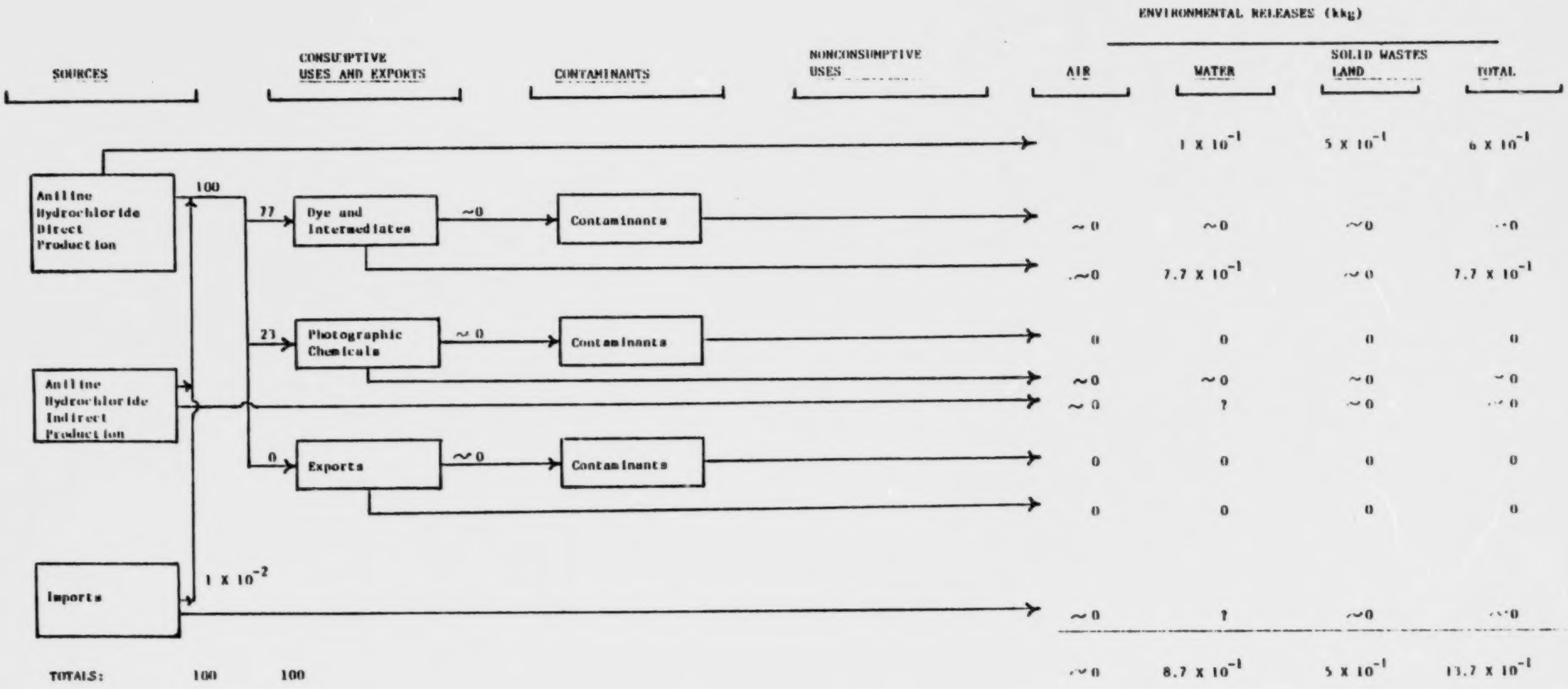
All anilines were produced in the eastern half of the U.S., with the greatest concentrations of aniline capacity along the east coast and Gulf coast.

This report contains many best-judgement estimates of important numbers. Production and consumption data for nitroanilines, haloanilines, and aniline hydrochloride will be required for meaningful emissions estimates for these classes. Another key quantity that was missing was a documented aqueous waste stream analysis for an aniline production plant. These data will be necessary for more detailed analysis of aniline emissions.

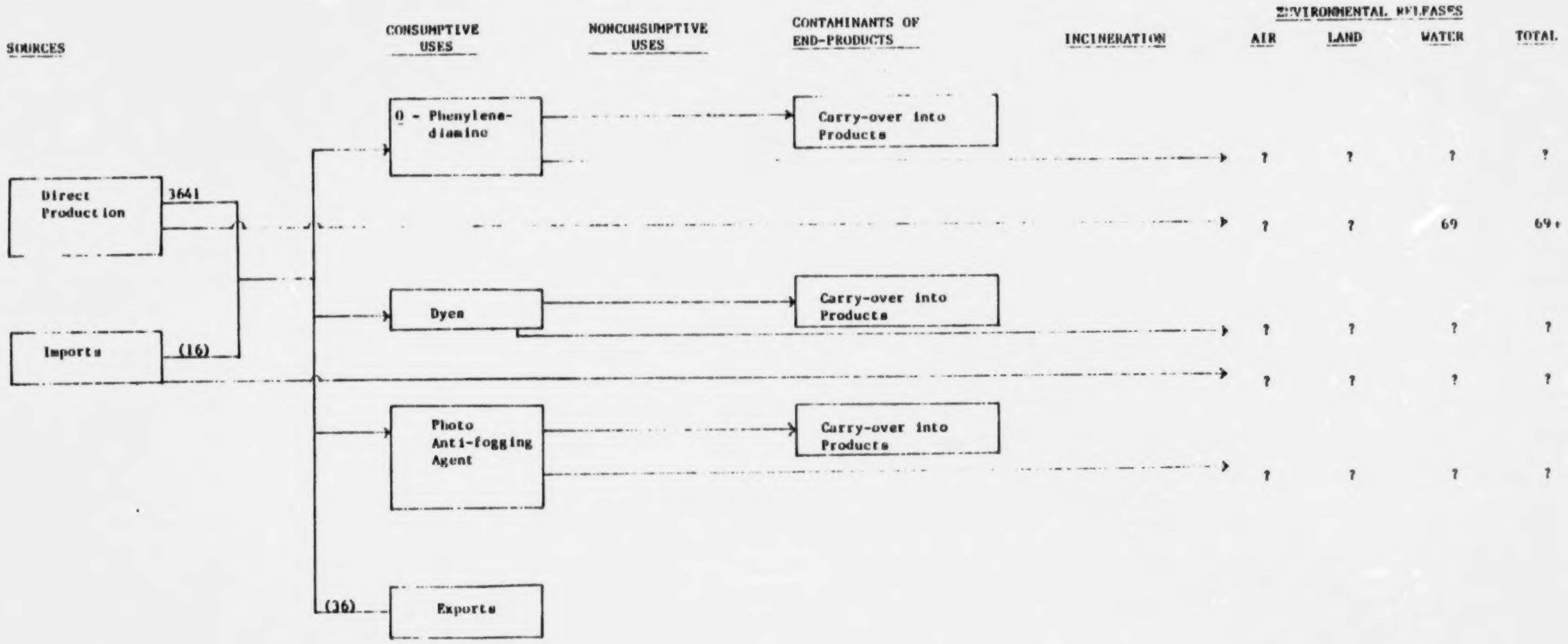
ES-1 MATERIALS BALANCE FOR ANILINE (KKG)


SOURCES
CONSUMPTIVE USE
NON-CONSUMPTIVE USE
CONTAMINANTS OF END-PRODUCTS
INCINERATION
EMISSIONS
AIR
LAND
WATER
TOTAL
Direct Production
279,000
Imports
1
Indirect Production (product breakdown; oil; auto exhaust)
?
148,000
Isocyanate Production
Carry-over
19
?
3700
3719
20
?
65.6
26
80,000
Rubber Chemicals
Carry-over
Aniline Hydrobromide
20
?
3900
3920
4 X 10⁻⁶
0
6.3 X 10⁻⁸
4 X 10⁻⁶
15,000
Hydroquinone
Carry-over
4
?
700
704
9,000
Drugs
Carry-over
Acetanilide for Drugs
0
?
85
85
18,000
Dyes and Intermediates
Carry-over
Aniline Hydrochloride
4
?
900
904
2,800
Exports
2 X 10⁻⁵
0
2 X 10⁻⁴
2 X 10⁻⁴
27,000
Miscellaneous Chemicals fibers, herbicides)
Carry-over
Acetanilide/ P-Nitroaniline
3
?
700
703
TOTALS:
279,000
300,000
70
?
10,000
10,070

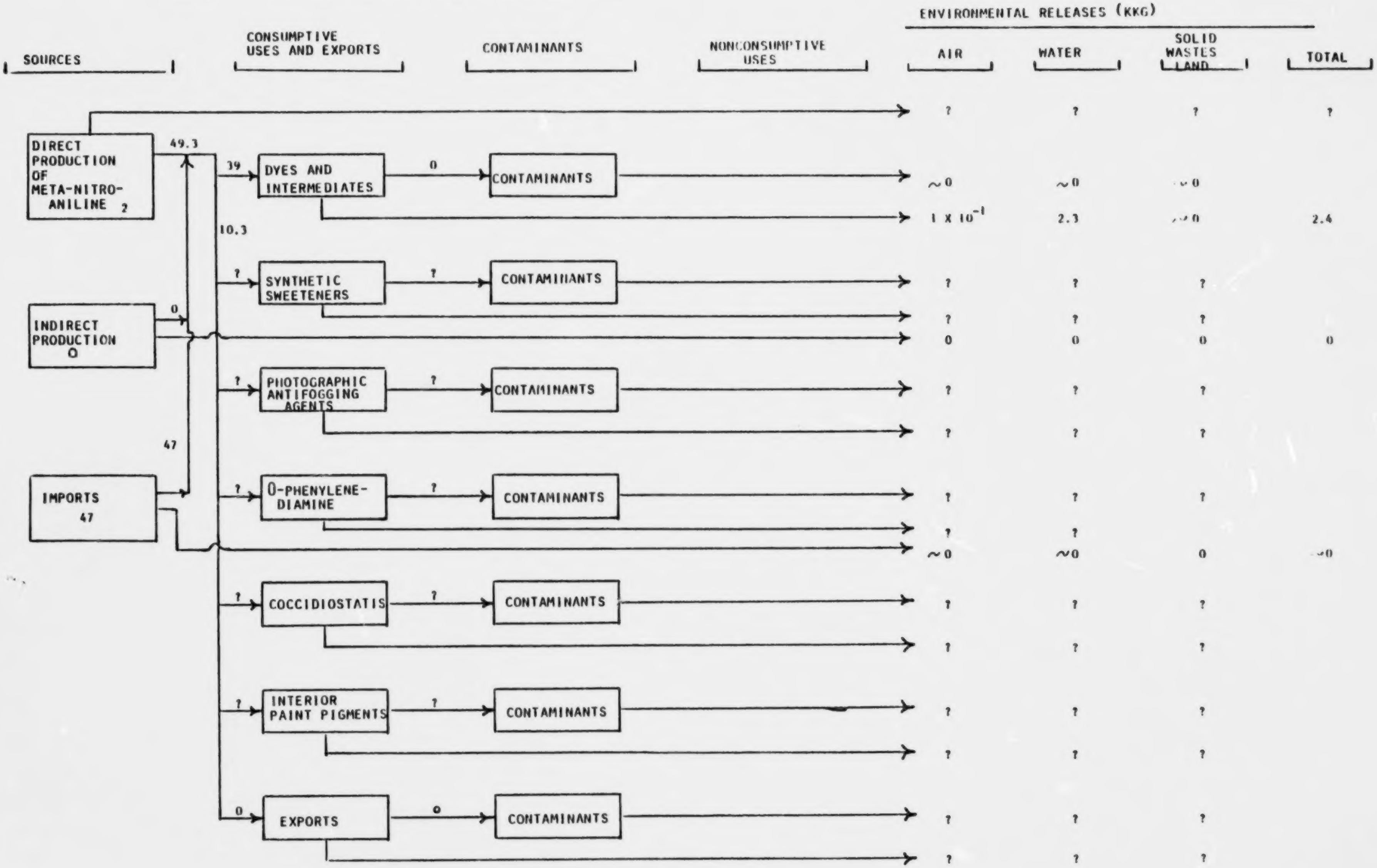
ES-2 1978 MATERIALS BALANCE FOR ANILINE HYDROCHLORIDE (KKG)


ENVIRONMENTAL RELEASES (kkg)
SOURCES
CONSUMPTIVE USES AND EXPORTS
CONTAMINANTS
NONCONSUMPTIVE USES
AIR
WATER
SOLID WASTES LAND
TOTAL
Aniline Hydrochloride Direct Production
Aniline Hydrochloride Indirect Production
Imports
100
77
23
0
1 x 10⁻²
Dye and Intermediates
Photographic Chemicals
Exports
~0
~0
~0
Contaminants
Contaminants
Contaminants
1 x 10⁻¹ | 5 x 10⁻¹ | 6 x 10⁻¹
~0 | ~0 | ~0 | ~0
~0 | 7.7 x 10⁻¹ | ~0 | 7.7 x 10⁻¹
0 | 0 | 0 | 0
~0 | ~0 | ~0 | ~0
~0 | ? | ~0 | ~0
0 | 0 | 0 | 0
0 | 0 | 0 | 0
~0 | ? | ~0 | ~0
TOTALS: 100 100
~0 | 8.7 x 10⁻¹ | 5 x 10⁻¹ | 13.7 x 10⁻¹

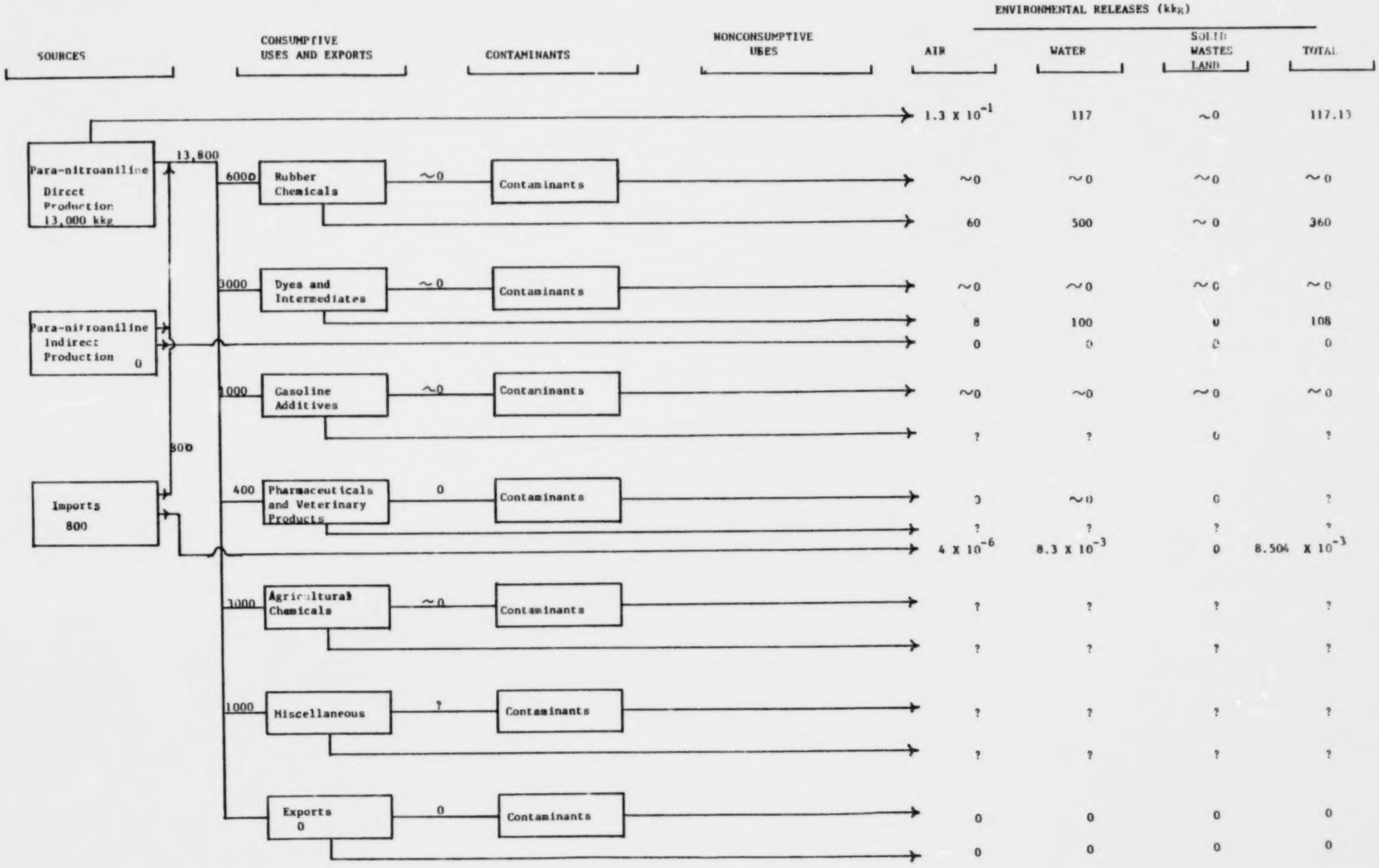
ES-3 MATERIALS BALANCE FOR O - NITROANILINE (KKG)


SOURCES
CONSUMPTIVE USES
NONCONSUMPTIVE USES
CONTAMINANTS OF END-PRODUCTS
INCINERATION
ENVIRONMENTAL RELEASES
AIR
LAND
WATER
TOTAL
Direct Production
3641
Imports
(16)
O - Phenylene-diamine
Carry-over into Products
?
?
?
?
?
?
69
69+
Dyes
Carry-over into Products
?
?
?
?
?
?
?
?
Photo Anti-fogging Agent
Carry-over into Products
?
?
?
?
(36)
Exports

ES-4 MATERIALS BALANCE FOR m-NITROANILINE (kkg)


ENVIRONMENTAL RELEASES (kkg)
SOURCES
CONSUMPTIVE USES AND EXPORTS
CONTAMINANTS
NONCONSUMPTIVE USES
AIR
WATER
SOLID WASTES LAND
TOTAL
DIRECT PRODUCTION OF META-NITRO-ANILINE 2
INDIRECT PRODUCTION 0
IMPORTS 47
49.3
0
47
39
10.3
DYES AND INTERMEDIATES
SYNTHETIC SWEETENERS
PHOTOGRAPHIC ANTIFOGGING AGENTS
O-PHENYLENE-DIAMINE
COCCIDIOSTATIS
INTERIOR PAINT PIGMENTS
EXPORTS
CONTAMINANTS
? ? ? ?
~0 ~0 ~0
1 x 10^-1 2.3 ~0 2.4
? ? ?
? ? ?
0 0 0 0
? ? ?
? ? ?
? ? ?
? ?
~0 ~0 0 ~0
? ? ?
? ? ?
? ? ?
? ? ?
? ? ?
? ? ?

ES- 5 MATERIALS BALANCE FOR p-NITROANILINE (KKG)


ENVIRONMENTAL RELEASES (kkg)
SOURCES
CONSUMPTIVE USES AND EXPORTS
CONTAMINANTS
NONCONSUMPTIVE USES
AIR
WATER
SOLID WASTES LAND
TOTAL
Para-nitroaniline Direct Production 13,000 kkg
Para-nitroaniline Indirect Production 0
Imports 800
13,800
800
6000
Rubber Chemicals
~0
3000
Dyes and Intermediates
~0
1000
Gasoline Additives
~0
400
Pharmaceuticals and Veterinary Products
0
3000
Agricultural Chemicals
~0
1000
Miscellaneous
?
Exports 0
0
Contaminants
1.3 X 10^-1 117 ~0 117.13
~0 ~0 ~0 ~0
60 500 ~0 360
~0 ~0 ~0 ~0
8 100 0 108
0 0 0 0
~0 ~0 ~0 ~0
? ? 0 ?
0 ~0 0 ?
? ? ? ?
4 X 10^-6 8.3 X 10^-3 0 8.504 X 10^-3
? ? ? ?
? ? ? ?
? ? ? ?
? ? ? ?
0 0 0 0
0 0 0 0

1.0 INTRODUCTION

This report was prepared in response to a task order from the U.S. Environmental Protection Agency (EPA) for a Phase I materials balance study on anilines. The study includes the compounds aniline, aniline hydrochloride, aniline hydrobromide, o-, m-, and p-nitroaniline, plus several other chloro-, bromo-, and nitro- derivatives. The EPA was primarily concerned with possible sources of release to the environment and the amounts involved, since the compounds are highly toxic. These substances can be absorbed through skin, ingested, or inhaled (Hawley, 1977; TRW, 1973a).

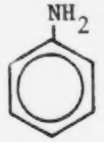
In order to present efficiently the data on many different but related compounds, each compound being studied was the topic of a separate chapter. Within each chapter were sections on emissions due to production, consumption, and other processes. Tables and figures showing 1978 data were interspersed in the text, but data for other years were presented at the end of each chapter.

In the tables reporting "releases" (emissions) data, the term "releases to soil" was defined as "material applied to the soil," as opposed to material applied to a landfill. A landfill was interpreted as a form of waste storage rather than as a sink. The rationale was that anilines in solid form in a landfill are lost to water through leaching or to air through slow evaporation. These generalizations were particularly true of aniline itself. Thus, the lack of entries in a "releases to soil" column only means that if aniline-containing solids were placed in a landfill, the amount of aniline present would have been apportioned to air and water to reflect long-term reality. On the other hand, actual "release to soil" would include use of pesticides, fertilizers, or other chemicals that would yield aniline due to microbial or photochemical degradation. Such releases would be tabulated as sources of aniline.

2.0 ANILINE

2.1 PHYSICAL PROPERTIES

The compound aniline (aminobenzene) is the parent compound for many of the 40 anilines to be studied in this report. It is a liquid at room temperature. Its physical properties can be summarized as follows: (Hawley, 1977; Weast, 1977-78; Strecher, 1968):



Aniline

Mol. Wt. 93.13

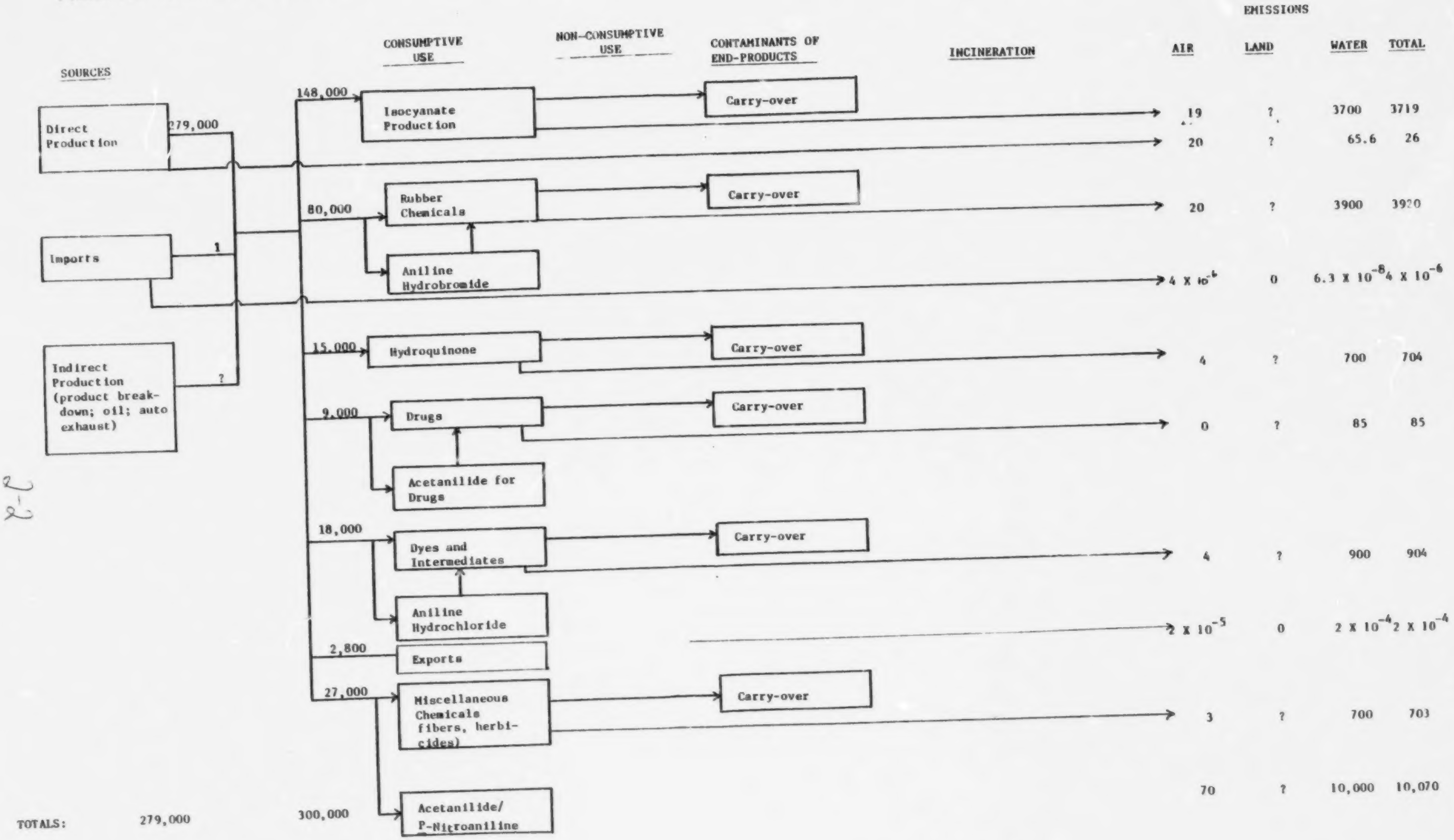
Melting point	-6.2°C
Boiling point	184.4°C
Solubility in Cold H_2O	35 g/l (0.38 M)
Solubility in Boiling H_2O	64 g/l (0.68 M)
Temperature at which vapor pressure = 1 Torr	34.8°C
pKa	4.63

Of particular interest are aniline's water solubility and vapor pressure. Aniline is soluble even in cold water. Its vapor pressure is low compared, for instance, to toluene (1 Torr at -92°C) and benzene (1 Torr at -58°C).

2.2 MATERIALS BALANCE FOR ANILINE

Figure 2.1 shows the materials balance for aniline. It demonstrates the sources of aniline (production, imports), the consumptive and non-consumptive uses of aniline (e.g., isocyanate production), and the estimated emissions to air, land, and water due to each process. This materials balance diagram is for the most recent year for which reasonably complete data are available: 1978. The purpose of this chapter is to explain the assumptions and calculations that yielded the values reported in the figure.

FIGURE 2.1 MATERIALS BALANCE FOR ANILINE (KKG)



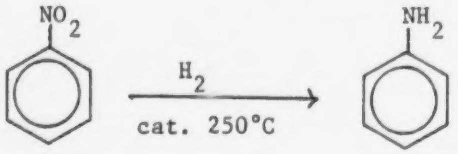
EMISSIONS
SOURCES
CONSUMPTIVE USE
NON-CONSUMPTIVE USE
CONTAMINANTS OF END-PRODUCTS
INCINERATION
AIR
LAND
WATER
TOTAL
Direct Production
279,000
Imports
1
Indirect Production (product breakdown; oil; auto exhaust)
?
148,000
Isocyanate Production
Carry-over
19
?
3700
3719
20
?
65.6
26
80,000
Rubber Chemicals
Carry-over
20
?
3900
3920
Aniline Hydrobromide
4 X 10^-6
0
6.3 X 10^-8
4 X 10^-6
15,000
Hydroquinone
Carry-over
4
?
700
704
9,000
Drugs
Carry-over
0
?
85
85
Acetanilide for Drugs
18,000
Dyes and Intermediates
Carry-over
4
?
900
904
Aniline Hydrochloride
2 X 10^-5
0
2 X 10^-4
2 X 10^-4
2,800
Exports
27,000
Miscellaneous Chemicals fibers, herbicides)
Carry-over
3
?
700
703
Acetanilide/ P-Nitroaniline
70
?
10,000
10,070
TOTALS:
279,000
300,000

2.3 DIRECT PRODUCTION OF ANILINE

The processes by which aniline is produced were divided into direct (or planned) production and indirect production. This section discusses direct production of aniline.

2.3.1 Production Processes, Producers, and Locations

Aniline can be synthesized industrially by the vapor-phase reduction of nitrobenzene or by ammonolysis of chlorobenzene (TRW Systems Group, 1973b). However, the Stanford Research Institute Chemical Economics Handbook (McCaleb, 1979) cites only the nitrobenzene reduction process as the current method of aniline synthesis. Therefore, it was assumed that at least 95% of aniline production takes place by the process:



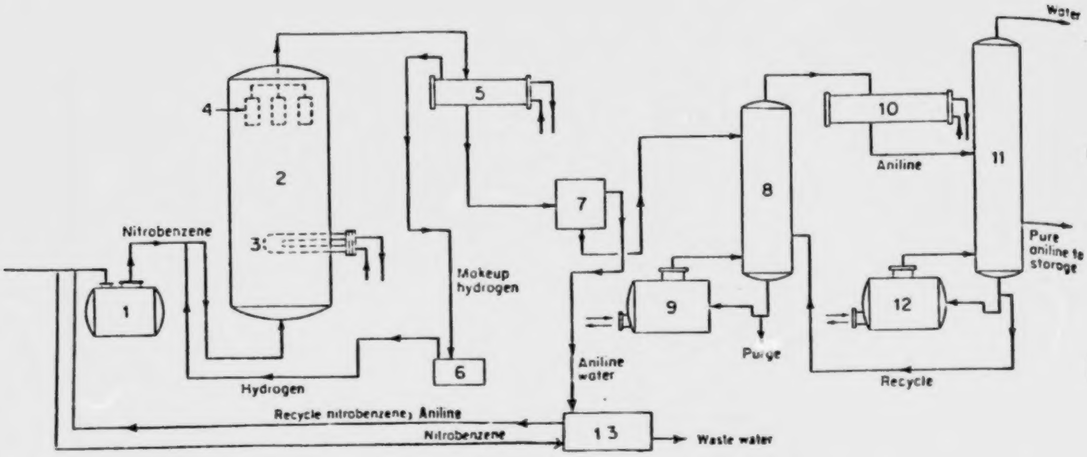
Nitrobenzene Aniline

The process flow for catalytic vapor-phase hydrogenation of nitrobenzene is in Figure 2.2 (Syracuse Research Corp., 1976). A more complete description of the process is found in Appendix A. The hydrogenation is carried out in the vapor phase (i.e., the temperature is greater than 211°C, the boiling point of nitrobenzene).

The locations of aniline production sites and each plant's capacity are shown in Figure 2.3. The seven production plants are all in the eastern half of the country, with two in New Jersey, two in West Virginia, and three on the Gulf Coast.

FIGURE 2.2

CATALYTIC VAPOR-PHASE HYDROGENATION OF NITROBENZENE


Water
5
4
2
3
Nitrobenzene
1
Makeup hydrogen
6
Hydrogen
Recycle nitrobenzene, Aniline
Nitrobenzene
13
Waste water
7
Aniline water
8
9
Purge
10
Aniline
11
Pure aniline to storage
12
Recycle

1. Nitrobenzene vaporizer.
2. Reactor with fluidized catalyst bed.
3. Cooling tubes.
4. Catalyst filters.
5. Product condenser.
6. Hydrogen recycle compressor.
7. Aniline—water settler and decanter.
8. Crude aniline still.
9. Reboiler for crude aniline still.
10. Condenser.
11. Aniline-finishing still.
12. Reboiler for aniline-finishing still.
13. Counter-current extraction column for aniline-water.

2.3.2 Amounts Produced

Data were available on the production of aniline for the past several years. The amount of aniline produced in 1978 was estimated to be 279,000 kkg. This value was selected from the data presented in Figure 2.3 on the basis of the following:

1) Partial USITC production data for 1979 showed that for the eight months from January through August, 1979, 195,416 kkg of aniline were produced.

2) The monthly production values showed no discernable trend, so annual production was estimated by linear extrapolation of the 8-month production: (195,416 kkg/8 mo.) x (1.5) = 293,000 kkg/12 mos. predicted for 1979.

3) In order to estimate the 1978 production, equal growth rates were assumed for 1977-1978 and 1978-1979. The estimated 1978 production was:

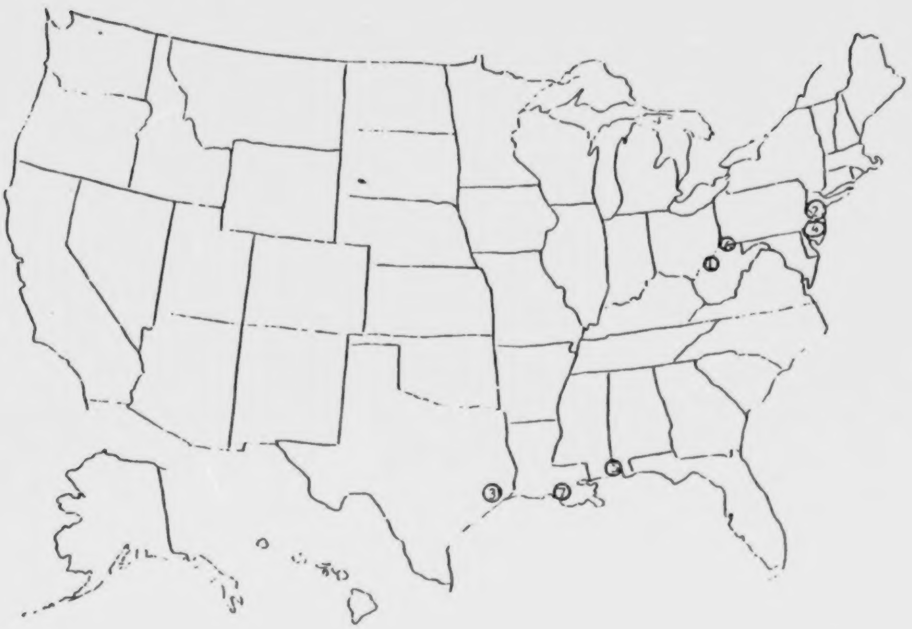
$$(1977\ \text{production}) + \frac{(1979\ \text{prod.}) - (1977\ \text{prod.})}{2};$$

$$\text{estimated 1978 production} = 265{,}000 + \frac{293{,}000-265{,}000}{2} = 279{,}000\ \text{kkg produced}$$

in 1978. Even though this value was based on estimated productions, it was

FIGURE 2.3 PRODUCTION OF ANILINE (kkg)

LOCATIONS



PRODUCTION[1]

MBER N MAP	PRODUCER AND LOCATION	PROCESS[2]	1978 PRODUCTION	1977 PRODUCTION	1976 PRODUCTION	1975 PRODUCTION	1974 PRODUCTION	PREDICTED 1980 PRODUCTION	REMARKS
1	American Cyanamid, Willow Island, WV	Hydrogenation of nitrobenzene	23,000	23,000	23,000	23,000		23,000	
2	American Cyanamid Bound Brook, NJ[3]	Hydrogenation of nitrobenzene						27,000	
3	E.I. duPont de Nemours Beaumont, TX	Hydrogenation of nitrobenzene	105,000	105,000	105,000	105,000		118,000	Most is used captively fe dyes, rubber chemicals, ag. chemical
4	duPont Gibbstown, NJ	Hydrogenation of nitrobenzene	60,000	60,000	60,000	60,000		73,000	
5	First Chemical Corp. Pascagoula, MS	Hydrogenation of nitrobenzene	115,000	45,000	45,000	45,000		115,000	Produced for sale
6	Mobay Corp. New Martinsville, WV	Hydrogenation of nitrobenzene	45,000	45,000	45,000	45,000		45,000	Used captively for poly urethanes
7	Rubicon Corp. Geismar, LA	Hydrogenation of nitrobenzene	27,000	27,000	25,000	25,000		127,000	Used captively for poly urethanes
	SUM:		375,000	305,000	303,000	303,000		528,000	
	USITC TOTAL			265,000	247,000	185,000	250,000		
	SRI TOTAL[4]		275,000						

1. McCaleb, (1979). Estimates based on plant capacities.
2. Catalytic, Inc. (1978).
3. According to McCaleb (1979), aniline production is scheduled to begin during 1978 after being shut down since 1974.
4. McCaleb (1979). Preliminary estimate based on aniline consumption.

still a more valid production value than the sum of plant capacities because it was bracketed by two production values. We estimated that the 1979 estimated production was within 10% of what the true yearly total will be. The uncertainty associated with the estimated 1978 production was estimated to be ±20%, based on possible variation in the 1979 production value and a possible deviance from the growth rate extrapolation between 1977 and 1979. As noted in the Remarks column, three production plants used their aniline captively, that is, the aniline was used as a feedstock for another process in the same plant. At least 177,000 kkg of capacity was dedicated to captive use in 1978. This was 47% of total capacity. On the basis of this, it was estimated that 47% of actual production was also used captively. The amount estimated to have been used captively was (279,000 kkg) x (0.47) = 132,000 kkg. Lowenheim and Moran (1975) estimated that, in general, about 60% of aniline production was used captively. USITC requires reporting of all aniline production greater than 2.3 kkg/year, whether it was captively used or not.

As the McCaleb (1979) estimate of 1980 production shows (Figure 2.3), a significant increase in aniline production is expected. This is due largely to a projected increase in use of aniline for isocyanate synthesis. Increases in the capacities of duPont's Beaumont, Texas, and Biggstown, New Jersey, plants; First Chemical's increase; and Rubicon's expasnion have been responses to this increased demand.

2.3.3 Emissions Due to Direct Production

2.3.3.1 Generated Emissions to Air

Overall emissions of aniline to air during production were considered to be the sum of emissions due to the production process itself + those due to product storage + those due to product transport. Data on emission amounts were not readily available for any of these steps. We therefore estimated the amounts of generated emissions to air by using the following operation for each step: (kkg produced, stored, or transported) x (emission factor in kkg/kkg) = kkg released due to production, storage, or transport. The estimated emissions to air calculated by this process were: 19 kkg/yr generated during production; 1.1 kkg/yr generated due to storage; and 7×10^{-4} kkg/yr released during transport. The total generated emission due to direct production was 20 kkg in 1978. The emission factors used to estimate these amounts are summarized in Table 2.1.

TABLE 2.1 EMISSION FACTORS FOR ANILINE RELEASE TO THE AIR DUE TO PRODUCTION

PROCESS	EMISSION FACTOR
Production	6.9×10^{-5} kkg/kkg (generated emissions)
Cleaning	?
Storage	4×10^{-6} kkg/kkg (generated emissions)
Transport	7×10^{-9} kkg/kkg (actual emissions)
Disposal	?

Aniline can be released to the air during the following steps in the production process (see Figure 2.2): leaks at connections and pumps; carry-over at finishing still vent. The emissions factor for production was obtained from direct data on air emissions at the Beaumont, Texas, aniline plant of duPont. (Hydroscience, Inc., 1977.) We estimated its uncertainty to be ±20% (their complete report is due at the end of December, 1979). In applying this emission factor to yearly production, we assumed the following: 1) All of the aniline produced in 1978 was synthesized by hydrogenation of nitrobenzene. 2) All plants carrying out this process have components and emission sources similar to those at the Beaumont plant. Emissions to air during production were estimated to be:

$$(279{,}000 \text{ kkg/yr}) \times (6.9 \times 10^{-5} \text{ kkg/kkg}) = 19 \text{ kkg/yr}$$

Taking into account the combined uncertainties of the production value and the emission factors, we estimated the uncertainty of the amount of emissions generated to be ±30%.

The emission factor for storage was obtained from plant data by Hydroscience, Inc. (1977). We estimated its uncertainty to be ±20%. In applying this emission factor to the amount of aniline stored, we assumed the following: 1) All aniline plants store the same fraction of their product as the Beaumont, Texas, duPont plant for which the emission factor was estimated. The amount of emissions generated due to storage was: (279,000 kkg) x (4 x 10^{-6} kkg/kkg) = 1.1 kkg of generated emissions to air due to storage in 1978.

The emission factor for losses due to transport was 7 x 10^{-9} kkg/kkg. It was estimated by using a model a study of spill/release risk in the petroleum industry (U.S. Coast Guard, 1973-1976; U.S. Army Corps of Engineers, 1973-1976; Science Applications, Inc., 1977; Science Applications, Inc., 1978; U.S. Department of Energy, 1978). The bases for this application were: 1) The modes of transportation for oil and aniline were basically the same (pipes, barrels, tank cars). 2) The petroleum industry studies cited above predicted that approximately 7 x 10^{-6}% of the total product moved would be lost during transport and handling. 3) This loss was estimated to be divided 10% to air and 90% to water because of aniline's low vapor pressure, moderate solubility in water, and the likelihood that most spills would be cleaned up by hosing down the area before significant evaporation occurred. 4) The amount of aniline transported was zero for plants that used the aniline captively. Therefore, this amount of production was subtracted from the total in order to get the amount of aniline transported: 279,000 kkg produced - 132,000 kkg used captively = 147,000 kkg transported. The amount of emissions released to air due to transport of domestic aniline was: (147,000 kkg transported) x (7 x 10^{-8} kkg/kkg) x (0.10 fraction to air) = 1 x 10^{-3} kkg/year.

2.3.2.2 Generated Emissions to Water

Overall emissions of aniline to water during production were considered to be the sum of emissions due to the production process itself plus those due to product transport. Data on emission amounts during these processes were unavailable. However, emission factors were available for each category, and these were used to estimate respective emissions. The estimated emissions to water were: 0.08 - 5.6 kkg/year generated by the production process; and 1 x 10^{-2} kkg/yr released during transport. The sum of these contributions was 0.09 - 5.6 kkg generated during aniline direct production for release to water during 1978.

In each case, the following operation was applied: (kkg produced or transported) x (emission factor in kkg/kkg) = kkg of emissions generated or released.

Aniline may be released to water at the following points during its production by hydrogenation of nitrobenzene (see Figure 2.2): Leaks at connections and pumps, purge valve of crude aniline still, condensate of final water boil-off in finishing still, waste water from extraction column. In the absence of direct data on water emissions, an estimate was derived from an estimated emission factor of 3×10^{-6} kkg/kkg. This value was based on the following: 1) MITRE Corp. (1978) cites the following data reported by two aniline manufacturers: Aniline release into the raw waste stream averaged 0.067 kg/kkg product. The range was 0.005 - 0.49 kg/kkg product, but there was no indication of the number of samplings included or who the manufacturers were. 2) This generated release factor would be lowered by effluent treatment. We estimated that 95% of aniline would be removed. 3) The discharged water, therefore, contained (6.7×10^{-5} kkg/kkg product) x (0.05 fraction not removed = 3×10^{-6} kkg/kkg product. This was the average emission factor for actual releases to water. The range of emission factors was 3×10^{-7} - 2×10^{-5} kkg/kkg produced.

Application of these emission factors to the estimation of emissions yielded: (279,000 kkg produced) x (3×10^{-6} kkg/kkg produced) = 0.84 kkg released to water due to aniline production in 1978. The range of values, calculated in the same way, was 0.08 - 5.6 kkg released.

The emission estimates spanned a range of 70-fold. The uncertainties of the minimum and maximum values were unknown. Statistical information on the effluent analyses that were the bases for the emission factors might be found in the primary source: EPA Organics and Plastics (1976), 308, Response BPR Master File Listing.

Because of the importance of this estimated emission to water, it should be checked for credibility by the following steps: 1) Probably the major source of aniline emissions to water is the wastewater effluent from the extraction column (process 13 in Figure 2.2). 2) The influent contains water saturated with aniline; therefore, the aniline concentration is approximately the physical limit: 35 g/l or 129 g/gal. 3) Assume the efficiency of the extraction column is 98% (Appendix A). 4) Obtain the yearly production of one or more plants. 5) Obtain the flow rates of effluent water from the respective extraction columns. 6) Calculate the emission factor for generated emissions (i.e., before treatment) in this waste stream by the operation: (129 x 10^{-5} kkg/gal influent) x (0.02 fraction in waste stream) x (annual waste stream volumes, gal) ÷ (annual production, kkg) = emission factor, kkg/kkg product. 7) Comparison of the value with the reported emission factor [avg. 6.7 x 10^{-5} kkg/kkg product in overall raw load (MITRE Corp., 1978)] would permit rough evaluation of consistency or inconsistency between the two emission factors.

Anilines may also be released to water during transport. No data were readily available on water emissions during transport. Therefore, the water emissions due to transport of aniline were estimated by the operation: (kkg aniline transported) x (emission factor, kkg released per kkg transported). The amount of emissions estimated by this procedure was 9 x 10^{-3} kkg/yr.

The emission factor used to obtain this estimate was 6.3 x 10^{-8} kkg/kkg transported. It was estimated by using as a model a study of spill/release risk in the petroleum industry (U.S. Coast Guard, 1973-1976; U.S. Army Corps of Engineers, 1973-1976; Science Applications, Inc., 1977; Science Applications, Inc., 1978; U.S. Department of Energy, 1978). The bases for this application were: 1) The modes of transportation for oil and aniline were basically the same (pipes, barrels, tank cars). 2) The petroleum industry studies cited above predicted that approximately 7 x 10^{-6}% of the total product moved would be lost during transport and handling. 3) This loss was estimated to be divided 10% to air and 90% to water because of aniline's low vapor pressure, moderate solubility in water, and the likelihood that most spills would be cleaned up by hosing down the area before significant evaporation occurred. 4) The amount of aniline transported was zero for plants that used the aniline captively. Therefore, this amount of production was subtracted from the total in order to get the amount of aniline transported: 279,000 kkg produced - 132,000 kkg used captively = 147,000 kkg transported. The amount of emissions released to water during transport of domestic aniline was (147,000 kkg transported) x (7 x 10^{-8} kkg/kkg) x (0.9 fraction to water) = 9 x 10^{-3} kkg/yr. This value was a low-side estimate because aniline is less vicous than oil and would therefore leak and spill more rapidly. We estimated the uncertainty for the release of aniline to water during transport to be +500%, -50%.

2.3.3.3 Emissions Due to Disposal of Solid Residues

Solid residue containing aniline could be produced at the following points in the flow scheme (Figure 2.2): walls of reactor; condenser surfaces; traps at bottom of crude and finished aniline stills; sludge from wastewater treatment. We estimated that these residues would contain negligible aniline. This was based on the following: 1) The solids were likely to be polymers and condensation products of aniline and/or nitrobenzene. Aniline would be a vapor or a liquid at operating temperatures. 2) Mechanically included aniline would be washed out of the residues by the gas or liquid flows across the residue.

In order to better evaluate the possibility of emissions in aniline-containing solids, the following are needed: 1) More detailed information on the production process (the nature of the trapped materials and other residues; 2) chemical analysis of residues; 3) rate of removal of residues; 4) methods of treatment for water wastes and solid residues.

2.4 INDIRECT PRODUCTION

2.4.1 Degradation of Products Derived from Anilines

Several of the compounds produced from anilines have the potential to yield anilines back by a simple reaction (usually either hydrolysis or oxidation). Examples would be hydrolysis of acetanilide or hydrolysis of phenyl isocyanates. Hydrolysis of even 0.01% of the 148,000 kkg of phenyl isocyanates produced in 1978 (see Table 2.4) would yield almost 15 kkg of aniline release. This possibility could be evaluated by studies on the rate of degradation of these compounds and their end-products.

2.4.2 Petroleum Industry

The following references in Chemical Abstracts might serve as a starting point for analysis in this area: (a) C.A. 89, abstract 149248g (1978), aniline in coal liquefaction products; (b) C.A. 89, abstract 113699r (1978), aniline in tar from underground coal gasification; (c) C.A. 89, abstract 48420b (1978), aniline in wastewater from coal gasification.

2.4.3 Automobile Exhaust

Phone conversations with EPA mobile emissions chemists lead to the suggestion that anilines are present at trace levels in automobile exhaust. Upper bounds on releases could be obtained from the operation: (detectability limit in ppb) x (kkg exhaust/yr.). This contribution (if any) may change as fuel consumption patterns change to synthetic or modified fuels with different nitrogen contents.

2.4.4 Hydrolysis of Acetanilide

Acetanilide is described as a "very widely used over-the-counter analgesic" (Casarett and Doull, 1975). One of its minor reactions *in vivo* is deacetylation to produce aniline (Casarett and Doull, 1975). By using annual consumption figures for acetanilide analgesics and biochemical data on proportion hydrolyzed or rate of hydrolysis, the amount of excreted aniline could be evaluated.

2.5 IMPORTS OF ANILINE

2.5.1 Amounts

The amounts of aniline imported were available in USITC publications for four of the last five years. Less than 1 kkg had been imported between January and August, 1978. Based on this, we estimated that 1 kkg of aniline was imported in 1978. The uncertainty of this value was estimated to be +50%, -25%. The other values available are presented in Table 2.2.

TABLE 2.2 IMPORTS OF ANILINE (kkg/year)

1978	1977	1976	1975	1974
1[1]	n.r.	n.r.	6288	9214

[1] For the months January through August, 1978 (McCaleb, 1979).

SOURCE: USITC. n.r. = not reported

The amount of aniline imported was variable, but was generally a small fraction of total production. The 1974 value, which was higher because of a domestic petroleum shortage due to the oil embargo, was 3.6% of production that year.

2.5.2 Emissions Due to Imports

2.5.2.1 Emissions to Air

Aniline can be released to the air during the storage and transport of imported aniline. These emissions are due to spills, leaks, and evaporation during transfer between containers. No data were available on the amounts of aniline lost to the air in these ways. We estimated that the emissions of aniline to the air during importing procedures was 4×10^{-6} kkg in 1978. This value was obtained by summing the contribution of emissions during transportation and handling (7×10^{-9} kkg/year) and the contribution of storage losses (4×10^{-6} kkg/year).

The emission factor used to estimate the emissions due to transportation and handling was 7×10^{-9} kkg/kkg imported. It was estimated by using as a model a study of spill/release risk in the petroleum industry (U.S. Coast Guard, 1973-1976; U.S. Corps of Engineers, 1973-1976; Science Applications, Inc., 1977; Science Applications, Inc, 1978; U.S. Department of Energy, 1978). The bases for this application were: 1) The modes of transportation for oil and aniline were basically the same (pipes, barrels, tank cars). 2) The petroleum industry studies cited above predicted that approximately 7×10^{-6}% of the total product moved would be lost during transport and handling. 3) This loss was estimated to be divided 10% to air and 90% to water because of aniline's low vapor pressure, moderate solubility in water, and the probability that most spills would be cleaned by hosing down the area before significant evaporation occurs. The emission factor estimated for release of aniline to air during transport and handling was $(7 \times 10^{-8}) \times (0.10) = 7 \times 10^{-9}$ kkg/kkg. Application of this emission factor to the amount of aniline imported in 1978 yielded: (1 kkg) x (7×10^{-9} kkg/kkg) = 7×10^{-9} kkg emitted to air during transport and handling of imports. This estimate represented a low-side value because aniline is significantly less viscous than oil and would therefore leak more rapidly than oil. We estimated the uncertainty of aniline emission at +500%, -50%.

The emission factor used to estimate emissions to air during storage was 4×10^{-6} kkg/kkg stored. This factor was estimated by Hydroscience, Inc. (1977). Pending an uncertainty estimate by the authors (their report is expected by the end of December, 1979), we estimated the uncertainty of the emission factor to be ±20%. In applying this emission factor to the estimation of aniline released to air during storage, we used the following basis: 1) The storage of imported aniline used the same equipment and procedures as the storage of domestic aniline. The amount of emissions to air due to storage of imported aniline was: (1 kkg) x ($4\ 10^{-6}$ kkg/kkg stored) = 4×10^{-6} kkg. Based on the uncertainties of the production data and the emission factor, the estimated uncertainty of the amount emitted during storage was +70%, -45%.

2.5.2.2 Emissions To Water

Emissions to water can occur during storage and transport of imported aniline. These releases are due to spills and leaks during transfer between containers. No data were available on emissions of aniline to water by these routes. It was estimated that the emissions of aniline to water during transport of imported aniline were 6.3×10^{-8} kkg in 1978.

The emission factor used to estimate the emissions due to transport was 6.3×10^{-8} kkg/kkg transported. This value was estimated by using as a model a study of spill/release risk in the petroleum industry (U.S. Coast Guard, 1973-1976; U.S. Army Corps of Engineers, 1973-1976; Science Applications, Inc., 1977; Science Applications, Inc., 1978; U.S. Department of Energy, 1978). The bases for this application were: 1) The modes of transportation for oil and aniline are basically the same (pipe, barrels, tank cars). 1) The petroleum industry studies cited above predicted that approximately 7×10^{-6}% of the total product moved would be lost during transport and handling. 3) This loss was estimated to be divided 10% to air and 90% to water because of aniline's low vapor pressure, moderate water solubility, and the likelihood that most spills would be cleaned up by hosing down the area before significant evaporation occurred. The amount of emissions to water during transport of imported aniline was: (1 kkg) x (7×10^{-8} kkg/kkg) x (0.9 fraction to water) = 6.3×10^{-8} kkg. This value was a low-side estimate because aniline is less viscous than oil and would therefore leak and spill more rapidly. We estimated the uncertainty for the release of imported aniline to water during transport to be +500%, -50%.

2.5.2.3 Emissions Due to Disposal of Solid Residues

It was estimated that the amount of solid residues accumulated as a result of aniline import was negligible, and that the release of aniline due to disposal of solid residues was zero.

2.5.3 Summary Table

Table 2.3 (end of chapter) summarizes the estimated emissions for years other than 1978. No import data were available for 1976.

2.6 CONSUMPTION AND USE OF ANILINE

Aniline is used in industry for the production of a variety of chemical substances. In all cases, it is a chemical intermediate (the starting point for further synthesis) rather than an end product itself. In general, there are three areas to examine for aniline emissions: 1) direct emissions during consumptive use, 2) carry-over as impurities in manufactured products, and 3) indirect emissions due to degradation of manufactured products.

2.6.1 Total Consumption

Data were available on the percentage of aniline production that was used in each of six major categories of use. In addition, the amount (kkg) of consumption by some categories was available. This permitted calculation of total consumption by the operation: (kkg used by a category) ÷ (fraction of total used by that category) = total consumption (kkg). The total consumption of aniline in 1978 was 296,000 kkg, based on the fact that the 148,000 kkg consumed in isocyanate synthesis represented 50% of total consumption (Chemical Marketing Reporter, 1979). The total consumption value estimated in this way is in parentheses in Figure 2.1. Above it is the amount of total available aniline. This amount was obtained by the process: (domestic production) - (emissions) - (exports) + (imports) = kkg aniline available for use. Possible explanations for the difference between the numbers (276,000 kkg available vs. 296,000 kkg consumed) are: 1) underestimation of imports, 2) overestimation of exports, 3) simple statistical variance: a change in the % contribution of isocyanate synthesis from 50% to 51% would lower the total aniline consumption by 6,000 kkg.

2.6.2 Categories of Use

The categories of aniline use, consuming companies, and amounts used for the past five years are presented in Table 2.4. The data were obtained from the footnoted references; we had no criterion on which to base an uncertainty estimate.

Isocyanate synthesis was the largest use category, and the trend was toward increasing aniline use by this category. Increases in isocyanate synthesis accounted for most of the increase in total aniline consumption over the past five years.

2.6.3 Use Within Each Category

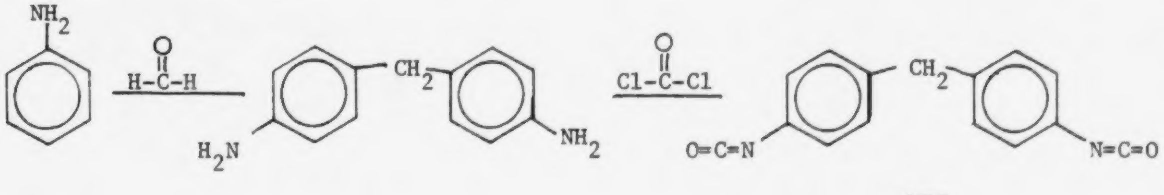
Tables 2.5 - 2.9 (end of chapter) provide a further breakdown of aniline use within the major categories. In the absence of direct data on use within each category, we estimated the breakdowns shown in the tables based on qualitative statements made in the chemical marketing literature. These estimates are described in the footnotes to the tables. Since emissions were calculated only for the major use categories, uncertainities in the breakdown percentages did not affect the emissions estimates.

An even more detailed listing of the derivatives of aniline, how they were produced, and how they were used is found in Appendix B.

2.6.4 Emissions by Category of Use

2.6.4.1 Emissions Due to Isocyanate Synthesis

Isocyanates can be formed by the reaction of amines with phosgene, $\mathrm{Cl{-}\overset{O}{\overset{\|}{C}}{-}Cl}$. Aniline is used to synthesize the bifunctional isocyanate p, p' - methylene-bis (phenylisocyanate), MDI. The reaction sequence is (McCaleb, 1979):



MDI

TABLE 2.4 INDUSTRIAL CONSUMPTION OF ANILINE, 1974-1978 (kkg/yr)

Category of Use	% of Aniline Consumption[2]	Company[1]	Product Classes[3]	Year	Amount Used (kkg)
isocyanate synthesis	50%	Mobay Chemical Corp. Rubicon Chemicals, Inc. Upjohn Co. Jefferson Chemical Co.	polymeric isocyanates urethane foams	1979	148,000[2]
				1977	132,000[4]
				1976	101,000[5]
				1975	78,000[5]
				1974	97,000[6]
Preparation of rubber chemicals	27%	American Cyanamid Co.	accelerators antioxidants antiozanants	1978	80,000[2]
				1977	83,000[4]
				1976	84,000[5]
				1975	65,000[5]
				1974	90,000[6]
manufacture of dyes	6%	American Cyanamid Co.	dyes and dye intermediates	1978	18,000[2]
				1977	13,000[4]
				1976	14,000[5]
				1975	11,000[5]
				1974	15,000[6]

TABLE 2.4 INDUSTRIAL CONSUMPTION OF ANLINE, 1974-1978 (continued)

Category of Use	% of Aniline Consumption	Company[1]	Product classes	Year	Amount Used (kkg)
hydroquinone production	5%	Tennessee Eastman Co.	antioxidants photodevelopers	1978	15,000[2]
				1977	13,000[4]
				1976	12,000[5]
				1975	9,000[5]
				1974	15,000[6]
drug manufacture	3%		sulfa drugs	1978	9,000[2]
				1977	8,000[4]
				1976	7,000[5]
				1975	6,000[5]
				1974	10,000[6]
miscellaneous (herbicides and (fibers)	9%		fibers herbicides other	1978	27,000[2]
				1977	13,000[4]
				1976	22,000[5]
				1975	17,000[5]
				1974	22,000[6]

Footnotes (Table 2.4)

1. Partial list of larger users. Source: McCaleb, 1979.
2. Chemical Marketing Reporter, 1979
3. Hahn, 1970.
4. Chemical Purchasing, 1977.
5. Chemical Marketing Reporter, 1976.
6. Chemical and Engineering News, 1974.

MDI polymerizes to form polyurethanes.

2.6.4.1.1 Emission to Air

Direct data were not readily available on aniline emissions to air during isocyanate synthesis. A best-judgement estimate was made on aniline emissions during this process. The estimated amount of generated aniline emissions to air during MDI synthesis in 1978 was 19 kkg. This value was obtained in the absence of data on emission factors during MDI synthesis by using the estimated emission factor 1.25×10^{-4} kkg/kkg aniline consumed. The bases for estimating this emission factor were: 1) Only the first (aniline-consuming) step in MDI synthesis was considered. 2) As with many industrial reactions, the yield in the first step was considered to be 95%. 3) Of the unreacted 5% of input aniline, 50% was recovered for re-use. 4) The remaining 2.5% of input aniline was released 0.5 part to air, 99.5 parts to water--consistent with aniline's physical properties. The emission factor obtained was: (0.05 fraction of aniline unreacted) x (0.5 fraction of unreacted not recovered) x (0.005 fraction to air) = 1.25×10^{-4} kkg/kkg.

We estimated the uncertainty of this release to be +500%, -80% based on the following: 1) The estimated emission would be an over-estimate if the synthesis processes were more efficient than the estimates used. 2) The allotment of total losses to air and water could be as much as 5- fold off in either direction.

2.6.4.1.2 Emissions to Water

Direct data were not readily available on aniline emissions to water during MDI synthesis. A best-judgement estimate was made of aniline emissions during this process. The estimated amount of generated aniline emissions to water during isocyanate synthesis in 1978 was 3700 kkg. This value was obtained in the absense of data on emission factors during MDI synthesis by using the estimated emission factor 2.5×10^{-2} kkg/kkg aniline used. The basis for estimating this emission factor was given in section 2.6.4.1.1. It was calculated as follows: (0.05 fraction of unused aniline) x (0.5 fraction of unused aniline not recovered) x (0.995 fraction of unrecovered aniline in water stream) = 2.5×10^{-2} kkg/kkg. The amount of aniline emissions generated was (148,000 kkg consumed) x (2.5×10^{-2} kkg/kkg) = 3700 kkg aniline emissions to water generated due to isocyanate synthesis in 1978.

Based on the reasoning described in section 2.6.4.1.1, the uncertainty of this emission value was estimated to be +500%, -80%.

2.6.4.1.3 Emissions Due to Disposal of Solid Residues

No direct data nor data on emission factors was available to permit estimation of emissions due to disposal of solid, aniline-containing residues formed during isocyanate synthesis. In order to be able to estimate emissions to air, land, and water due to this disposal, the following information would be needed: 1) process engineering information on the sources of residues during isocyanate synthesis; 2) quantitative analysis of the residues produced; 3) information on waste disposal methods at each plant (i.e., landfill, incineration, activated sludge treatment, stack gas scrubbers, etc.).

2.6.4.1.4 Carry-over of Aniline as Impurities in Products

No data were available to permit estimation of aniline emissions due to aniline impurities in isocyanates or polyurethanes derived from them. In order to estimate these emissions, the following information would be needed: 1) proprietary information on chemical analyses of the two predominant isocyanates manufactured; 2) chemical analyses of consumer goods containing aniline-based polyurethanes; 3) production data on the isocyanates and polymers involved.

2.6.4.1.5 Summary of Aniline Emissions Due to Isocyanate Synthesis

Table 2.10 (end of chapter) summarizes estimated emissions to air and water generated during isocyanate synthesis for the years 1974-1978. The table also breaks down total emissions into those due to MDI production and those due to polymethylene polyphenyldiisocyanate synthesis according to the estimated percent contribution shown in Table 2.5.

2.6.4.2 Emissions Due to Rubber Chemical Synthesis

Rubber chemicals synthesis utilized an estimated 80,000 kkg of aniline in 1978. This was 27% of total aniline usage (Table 2.4). Specific compounds and process flow schemes were not available for this category. Therefore, emissions were estimated for the generalized "process" of rubber chemicals production by the operation: (kkg aniline consumed) x (emission factor, kkg emissions/kkg aniline consumed) = kkg total generated emissions.

In the absence of data on either amounts of emissions or experimentally-determined emission factors, an overall best-judgement emission factor for generated emissions due to rubber chemicals synthesis was estimated. The value estimated was 5 x 10^{-2} kkg/kkg. This emission factor was for the sum of generated air emissions + generated water emissions. It was based on the following considerations: 1) In any chemical-synthesizing process, only the first (i.e., aniline-consuming) step was of interest. 2) On the average, this first reaction would utilize 90% of the aniline feedstock. 3) Of the remaining 10% of input aniline, half was reclaimed and recycled. 4) The generated emissions of aniline were therefore 0.05 (or 5%) of aniline consumed: (0.10 fraction not used) x (0.50 fraction of unused not reclaimed) = 0.05 kkg generated/kkg aniline used.

2.6.4.2.1 Generated Emissions to Air

In the absence of data on air emissions or emission factors during rubber chemical synthesis, we used the estimated emission factor above (5 x 10^{-2} kkg/kkg) to estimate the generated emissions to air during this process. The additional assumption required was: 1) Total generated emissions were distributed 0.5 part to air and 99.5 parts to water. The estimated emissions were: (80,000 kkg aniline used) x (5 x 10^{-2} kkg/kkg used) x (0.005 fraction to air) = 20 kkg generated for release to air during rubber chemicals production in 1978.

The uncertainty of this value was estimated to be +500%, -80%, based on the analysis presented in section 2.6.4.1.1.

2.6.4.2.2 Generated Emissions to Water

The method of estimating generated emissions to water during rubber chemical synthesis was the one described in section 2.6.4.2.1 (above) with the following exception: since 99.5% of total emissions were estimated to enter water waste, the value 0.995 replaces 0.005 in the calculation. The estimated emissions were: (80,000 kkg aniline used) x (5 x 10^{-2} kkg/kkg used) x (0.995 fraction to water) = 4000 kkg generated for release to water during rubber chemicals production in 1978. The uncertainty is estimated to be +500%, -80% (see section 2.6.4.1.1).

2.6.4.2.3 Emissions Due to Disposal of Solid Residues

No direct data nor data on emission factors were available to permit estimation of emissions due to disposal of solid, aniline-containing residues formed during rubber chemicals synthesis. In order to be able to estimate emissions to air, land, and water due to this disposal, the following information would be needed: 1) process engineering information on the sources of residues during specific synthesis steps utilizing aniline as a feedstock; 2) data on the percent contributions of the individual processes to the total for the rubber chemicals category; 3) quantitative analysis of residues produced; 4) rate of production of residues; 5) information on waste disposal methods at each plant (i.e., landfill, incineration, activated sludge treatment, stack gas scrubbers, etc.).

2.6.4.2.4 Carry-over of Aniline as Impurities in Products

No data were available to permit estimation of aniline emissions due to aniline impurities in rubber chemicals. In order to estimate these emissions, the following information would be needed: 1) identities and amounts of rubber chemicals derived from aniline; 2) chemical analyses of these rubber chemical batches.

2.6.4.2.5 Summary of Aniline Emissions Due to Rubber Chemicals Synthesis

Table 2.11 (end of chapter) summarizes estimated emissions to air and water generated during rubber chemicals synthesis for the years 1974-1978. The table also breaks down total emissions into subcategories: accelerators, antioxidants, antiozonants, and curing agents by using the estimated percent contributions shown in Table 2.6

2.6.4.3 Emissions Due to Manufacture of Dyes and Dye Intermediates

Dye and dye intermediate synthesis consumed an estimated 18,000 kkg of aniline in 1978. This was 6% of total aniline usage (Table 2.4). Specific products and process flow schemes were not available for this category. Therefore, emissions were estimated for the generalized "process" of dye and dye intermediate synthesis by the operation: (kkg aniline consumed) x (emission factor, kkg emissions/kkg aniline consumed) = kkg total generated emissions.

In the absence of data on either amounts of emissions or experimentally-determined emission factors, an overall best-judgement emission factor for generated emissions due to dye synthesis was estimated. The value estimated was 5 x 10^{-2} kkg/kkg. This emission factor was for the sum of generated air emissions + generated water emissions. It was based on the following considerations: 1) In anv chemical-synthesizing process, only the first (i.e., aniline-consuming) step was of interest. 2) On the average, this first reaction would utilize 90% of the aniline feedstock. 3) Of the remaining 10% of input aniline, half was reclaimed and recycled. 4) The generated emissions of aniline were therefore 0.05 (of 5%) of aniline consumed: (0.10 fraction not used) x (0.05 fraction of unused not reclaimed) = 0.05 kkg generated/kkg aniline used.

2.6.4.3.1 Generated Emissions to Air

In the absence of data on air emissions or emission factors during dye synthesis, we used the estimated emission factor above (5 x 10^{-2} kkg/kkg) to estimate the generated emission to air during this process. The additional assumption required was: 1) Total generated emissions were distributed 0.5 part to air and 99.5 parts to water. The estimated emissions were: (17,800 kkg aniline used) x (5 x 10^{-2} kkg/kkg used) x (0.005 fraction to air) = 4 kkg generated for release to air during dye production in 1978.

The uncertaintiy of this value was estimated to be +500%, -80%, based on the analysis presented in section 2.6.4.1.1.

2.6.4.3.2 Generated Emissions to Water

The method of estimating generated emissions to water during dye synthesis was the one described in section 2.6.4.3.1 (above) with the following exception: since 99.5% of total emissions were estimated to enter water waste, the value 0.995 replaced 0.005 in the calculation. The estimated emissions were: (17,800 kkg aniline used) x (5 x 10^{-2} kkg/kkg used) x (0.995 fraction to water) = 900 kkg generated for release to water during dye production in 1978. The uncertainty was estimated to be +500%, -80% (see section 2.6.4.1.1).

2.6.4.3.3 Emissions Due to Disposal of Solid Residues

No direct data nor data on emission factors were available to permit estimation of emissions due to disposal of solid, aniline-containing residues formed during dye synthesis. In order to be able to estimate emissions to air, land, and water due to this disposal, the following information would be needed: 1) process engineering information on the sources of residues during specific synthesis steps utilizing aniline as a feedstock; 2) data on the percent contributions of the individual processes to the total for the dyes category; 3) quantitative analysis of residues produced; 4) rate of production of residues; 5) information on waste disposal methods at each plant (i.e., landfill, incineration, activated sludge treatment, stack gas scrubbers, etc.).

2.6.4.3.4 Carry-Over of Aniline as Impurities in Products

No data were available to permit estimation of aniline emissions due to aniline impurities in dyes and dye intermediates. In order to estimate these emissions, the following information would be needed: 1) identities and amounts of dye chemicals derived from aniline; 2) chemical analyses of these dye chemical batches.

2.6.4.3.5 Summary of Aniline Emissions Due to Dye and Dye Intermediate Synthesis

Table 2.12 (end of chapter) summarizes estimated emissions to air and water generated during dye chemical synthesis for the years 1974-1978. The table also breaks down total emissions into subcategories: azoic, indigoid, stilbene, and triarylmethane dyes, and pre-dye treatments by using the estimated percent contributions shown in Table 2.7.

2.6.4.4 Emissions Due to Hydroquinone Production

Hydroquinone synthesis consumed an estimated 15,000 kkg of aniline in 1978. This was 5% of total aniline usage (Table 2.4). Hydroquinone is produced from aniline in a two-step process (Kirk-Othmer, 1968): the first step is the oxidation of aniline to quinone and the second step is the reduction of quinone to hydroquinone. Further production details were not available. Therefore, emissions were estimated by the operation: (kkg aniline used) x (emission factor, kkg emission/kkg aniline used) = kkg total generated emissions.

In the absence of data on either amounts of emissions or experimentally-determined emission factors, a best-judgement emission factor for generated emissions due to hydroquinone production was estimated. The value estimated was 5×10^{-2} kkg/kkg. This emission factor was for the sum of generated air emissions + generated water emissions. It was based on the following considerations: 1) In the two-step process mentioned above, the aniline-oxidizing step was judged to utilize 90% of aniline input. 2) Of the remaining 10% of aniline feedstock, half was reclaimed and recycled. 3) The generated emissions of aniline were therefore 0.05 (5%) of aniline consumed: (0.10 fraction not used) x (0.50 fraction of unused not reclaimed) = 0.05 kkg generated/kkg aniline used.

2.6.4.4.1 Generated Emissions to Air

In the absence of data on air emissions or emission factors during hydroquinone synthesis, we used the estimated emission factor above (5×10^{-2} kkg/kkg) to estimate the generated emissions to air during this process. The additional assumption required was: 1) Total generated emissions were distributed 0.5 part to air and 99.5 parts to water. The estimated emissions were: (14,800 kkg aniline used) x (5×10^{-2} kkg/kkg used) x (0.005 fraction to air) = 4 kkg generation for release to air during hydroquinone production in 1978.

The uncertainty of this value was estimated to be +500%, -80%, based on the analysis presented in section 2.6.4.1.1.

2.6.4.4.2 Generated Emissions to Water

The method of estimating generated emissions to water during hydroquinone synthesis was the one described in section 2.6.4.4.1 (above) with the following exception: since 99.5% of total emissions are estimated to enter water waste, the value 0.995 replaces 0.005 in the calculation. The estimated emissions were: (14,800 kkg aniline used) x (5 x 10^{-2} kkg/kkg used) x (0.995 fraction to water) = 700 kkg generated for release to water during hydroquinone production in 1978. The uncertainty is estimated to be +500%, -80% (see section 2.6.4.1.1).

2.6.4.4.3 Emissions Due to Disposal of Solid Residues

No direct data nor data on emission factors were available to permit estimation of emissions due to disposal of solid, aniline-containing residues formed during hydroquinone synthesis. In order to be able to estimate emissions to air, land, and water due to this disposal, the following information would be needed: 1) process engineering information on the sources of residues during the synthesis step utilizing aniline as a feedstock; 2) quantitative analysis of residues produced; 3) rate of production of residues; 4) information on waste disposal methods at each plant (i.e., landfill, incineration, activated sludge treatment, stack gas scrubbers, etc.).

2.6.4.4.4 Carry-Over of Aniline as Impurities in Products

No data were available to permit estimation of aniline emissions due to aniline impurities in hydroquinone. In order to estimate these emissions, the following information would be needed: 1) chemical analyses of hydroquinone batches.

2.6.4.4.5 Summary of Aniline Emissions Due to Hydroquinone Synthesis

Table 2.13 (end of chapter) summarizes estimated emissions to air and water generated during hydroquinone synthesis for the years 1974-1978.

2.6.4.5 Emissions Due to Drug Manufacture

Drug manufacture utilized an estimated 8900 kkg of aniline in 1978. This was 3% of total aniline usage (Table 2.4). With the exception of acetanilide synthesis, specific compounds and process flow schemes were not available for this category. Therefore, emissions were estimated for the generalized "process" of drug manufacture, excluding acetanilide-based drugs. In both cases, the estimation was obtained by the operation: (kkg aniline consumed) x (emission factor, kkg emissions/kkg aniline consumed) = kkg total generated emissions.

In the absence of data on either amounts of emissions or experimentally-derived emission factors, an overall best-judgement emission factor for generated emissions due to non-acetanilide-based drug synthesis was estimated. The value estimated was 9×10^{-3} kkg/kkg. This emission factor was for the sum of air emissions + water emissions. It was based on the following considerations: 1) Only the first (aniline-consuming) step in a multi-step drug synthesis was of interest. 2) In the drug industry, purity of product would be more important than recovery of yield. Therefore, the aniline-derivatizing reaction would be run in such a way as to minimize unused aniline accompanying the product. We estimated that 1% unused aniline was possible. 3) Of this 1% of input, all but 0.1% would be removed by subsequent purifications and emitted to waste streams. 4) The estimated overall emission factor was therefore (0.01 fraction of aniline unused) x (0.9 fraction of unused emitted) = 9×10^{-3} kkg/kkg aniline used.

The emission factor for acetanilide-based drug synthesis was estimated to be 1×10^{-2} kkg/kkg. This emission factor was for the sum of air emissions + water emissions. It was based on the following considerations: 1) Acetanilide synthesis would be made to use at least 99% of input aniline. 2) Analysis of technical grade acetanilide showed 0.2% aniline carryover (Kirk-Othmer, 1968). This corresponds to $(0.2\%) \times \left(\frac{135}{93}\right) = 0.3\%$ of input aniline (135 and 93 are the respective molecular weights of acetanilide and aniline). 3) Therefore, 0.7% of input aniline was emitted to water and air. 4) The 0.3% input aniline occurring as an impurity in technical grade acetanilide was removed during production of USP acetanilide, which contained no aniline (Kirk-Othmer, 1968). It was tabulated as an additional emission. The estimated overall emission factor was 1×10^{-2} kkg/kkg aniline used.

2.6.4.5.1 Emissions to Air

It was estimated that emissions to air were negligible during drug synthesis. This was because we judged that: 1) each aniline-derivatizing reaction would take place efficiently in aqueous solution, and 2) purification of drug intermediates often would involve crystallization of the desired compound and discarding of the separated impurities in the aqueous mother liquor.

2.6.4.5.2 Emissions to Water

As described in section 2.6.5.5.1 (above), all aniline emissions due to drug synthesis were considered to be aqueous emissions. The total aqueous emissions were the sum of emissions due to non-acetanilide synthesis plus acetanilide synthesis. In the absence of data on the relative contributions of these two processes to the total, we used a distribution of 50% aniline consumption by each route. The total emissions were estimated to be: [(0.50 fraction contribution) x (8900 kkg total aniline used) x (9 x 10^{-3} kkg/kkg used)] + [(0.50) x (8900 kkg) x (1 x 10^{-2} kkg/kkg)] = 40 kkg (non-acetanilide) + 45 kkg (acetanilide) = 85 kkg aniline generated for emission to water during drug synthesis.

The uncertainty of this emission was estimated to be +100%, -50% based on the following: 1) The emissions were relatively insensitive to changes in allocation between acetanilide and non-acetanilide drugs because the emission factors were similar in size. 2) The emission factors were estimated to be accurate to within a factor of 2 in each direction.

2.6.4.5.3 Emissions Due to Disposal of Solid Residues

No direct data on emission factors were available to permit estimation of emissions due to disposal of solid, aniline-containing residues formed during drug synthesis. In order to be able to estimate emissions to air, land, and water due to this disposal, the following information would be needed: 1) process engineering information on the sources of residues during specific synthesis steps utilizing aniline as a feedstock; 2) data on the percent contributions of the individual processes to the total for the drug category; 3) quantitative analysis of residues produced; 4) rate of production of residues; 5) information on waste disposal methods at each plant (i.e., landfill, incineration, activated sludge treatment, stack gas scrubbers, etc.).

2.6.4.5.4 Carry-Over of Aniline as Impurities in Products

It was estimated that aniline content in drugs derived from aniline would be zero, based on purity controls required in the pharmaceuticals industry.

2.6.4.5.5 Summary of Aniline Emissions Due to Drug Synthesis

Table 2.14 (end of chapter) summarizes estimated emissions to air and water generated during drug synthesis for the years 1974-1978.

2.6.4.6 Emissions Due to Miscellaneous Consumption

Synthesis of miscellaneous compounds consumed an estimated 27,000 kkg of aniline in 1978. This was 9% of total aniline usage (Table 2.4). With the exception of p-nitroaniline synthesis via acetanilide, specific compounds and process flow schemes were not available for this category. Therefore, emissions were estimated for the generalized "process" of miscellaneous chemicals production by the operation: (kkg aniline consumed) x (emission factor, kkg emissions/kkg aniline consumed) = kkg total generated emissions.

In the absence of data on either amounts of emissions or experimentally-determined emission factors, an overall best-judgement emission factor for generated emissions due to non-acetanilide-based miscellaneous chemicals synthesis was estimated. The value estimated was 5×10^{-2} kkg/kkg. This emission factor was for the sum of generated air emissions + generated water emissions. It was based on the following considerations: 1) In any chemical-synthesizing process, only the first (i.e., aniline consuming) step was of interest. 2) On the average, this first reaction would utilize 90% of the aniline feedstock. 3) Of the remaining 10% of input aniline, half was reclaimed and recycled. 4) The generated emissions of aniline were therefore 0.05 (or 5%) of aniline consumed: (0.10 fraction not used) x (0.50 fraction of unused not reclaimed) = 5×10^{-2} kkg generated/kkg aniline used.

The emission factor for acetanilide-based-p-nitroaniline synthesis was estimated to be 0.7×10^{-2} kkg/kkg. This emission factor was for the sum of air emissions + water emissions. It was based on the following considerations: 1) Acetanilide synthesis would be made to use at least 99% of input aniline.

2) Analysis of technical grade acetanilide showed 0.2% aniline carry-over (Kirk-Othmer, 1968). This corresponds to (0.2%) x ($\frac{135}{93}$) = 0.3% of input aniline (135 and 93 are the respective molecular weights of acetanilide and aniline). 3) Therefore, 0.7% of input aniline was emitted to water and air. 4) The 0.3% input aniline occurring as an impurity in technical grade acetanilide was removed as nitroaniline during subsequent nitration of the acetanilide. This would also be true of hydrolyzed acetanilide formed by the strongly acidic conditions of nitration. These were not tabulated as additional emissions. The estimated emission factor for the acetanilide synthesis step was 0.7 x 10^{-2} kkg/kkg aniline used.

2.6.4.6.1 Generated Emissions to Air

Emissions to air due to synthesis of miscellaneous chemicals were estimated to total 3 kkg in 1978. This estimate was obtained using the emission factors derived above (section 2.6.4.6) plus the following considerations: 1) In the absence of data on breakdown of consumption within the miscellaneous category, we assumed that 50% of the 27,000 kkg was used in non-acetanilide-based syntheses and 50% was used to synthesize p-nitroaniline via acetanilide. 2) Total emissions were distributed 0.5 parts to air and 99.5 parts to water. 3) For the reasons discussed in section 2.6.4.5.1, emissions to air during acetanilide synthesis were estimated to be zero. The estimated emissions to air were: (13,500 kkg aniline used) x (5 x 10^{-2} kkg/kkg) x (0.005 fraction to air) = 3 kkg of aniline emissions generated for release to air during miscellaneous chemicals synthesis in 1978.

The uncertainty of this value was estimated to be +500%, -80% based on the analysis presented in section 2.6.4.1.1.

2.6.4.6.2 Generated Emissions to Water

Total generated emissions to water were the sum of emissions due to non-acetanilide-based miscellaneous chemicals synthesis plus those due to p-nitroaniline synthesis via acetanilide. The bases for estimation of emissions are given in section 2.6.4.6.1. (above). The estimated emissions were: (13,500 kkg aniline used) x (0.05 kkg/kkg) x (0.995 fraction to water) = 700 kkg due to non-acetanilide-based miscellaneous chemicals syntheses; and

(13,500 kkg used) x (0.7 x 10^{-2} kkg/kkg) x (1.00 fraction to water) = 900 kkg due to acetanilide-based p-nitroaniline synthesis. The sum was 700 kkg + 900 kkg = 1600 kkg generated emissions to water during miscellaneous chemicals synthesis in 1978.

The uncertainty of each of these values was estimated to be +500%, -80% based on the analysis presented in section 2.6.4.1.1.

2.6.4.6.3 Emissions Due to Disposal of Solid Residue

No direct data nor data on emission factors was available to permit estimation of emissions due to disposal of solid, aniline-containing residues formed during miscellaneous chemicals synthesis. In order to be able to estimate emissions to air, land, and water due to this disposal, the following information would be needed: 1) process engineering information on the sources of residues during specific synthesis steps utilizing aniline as a feedstock; 2) data on the percent contributions of the individual processes to the total for the miscellaneous chemicals category; 3) quantitative analysis of residues produced; 4) rate of production of residues; 5) information on waste disposal methods at each plant (i.e., landfill, incineration, activated sludge treatment, stack gas scrubbers, etc.).

2.6.4.6.4 Carry-Over of Aniline as Impurities in Product

With the exception of acetanilide, no data were available to permit estimation of aniline emissions due to aniline impurities in miscellaneous chemicals. In order to estimate these emissions, the following information would be needed: 1) identities and amounts of miscellaneous chemicals derived from aniline; 2) chemical analyses of these miscellaneous chemical batches. In the case of acetanilide, it was estimated that the amount of aniline emissions due to carry-over would be zero. This was based on the judgement that even though technical grade aniline carries 0.2% aniline as an impurity (Kirk-Othmer, 1968), this aniline would not survive the subsequent nitration step and would be quantitatively converted to nitroanilines.

2.6.4.6.5 Summary of Aniline Emissions Due to Miscellaneous Chemicals Synthesis

Table 2.15 (end of chapter) summarizes estimated emissions to air and water generated during miscellaneous chemicals synthesis for the years 1974-1978. The table also breaks down total emissions into subcategories: pesticides, herbicides, resins, corrosion inhibitors, petroleum additives, and other uses by using the estimated percent contributions shown in Table 2.9.

2.6.4.7 Generated Emissions Due to Exports

2.6.4.7.1 Amount of Exports

Data were not available on the amount of aniline exported in 1978. McCaleb (1979) cites industry sources as estimating exports to be 1% of production in 1968. In the absence of contrary or confirmatory data, it was assumed that exports were 1% of production in 1978, also. The amount exported would be (279,000) x (0.01) = 2800 kkg. No criteria were available to aid in estimating the uncertainty of this value.

2.6.4.7.2 Emissions to Air

Emissions to air due to export were considered to be due entirely to transport of aniline. No data were available on amounts of emissions or on emission factors. Therefore, a best-judgement estimate was made using the operation: (kkg exported) x (emission factor, kkg released/kkg exported) = emissions to air due to export.

In the absence of data on emission factors, the emission factor for air emissions due to transport during export was estimated to be 7×10^{-9} kkg/kkg. It was estimated by using as a model a study of spill/release risk in the petroleum industry (U.S. Coast Guard, 1973-1976; U.S. Army Corps of Engineers, 1973-1976; Science Applications, Inc., 1977; Science Applications, Inc., 1978; U.S. Department of Energy, 1978). The bases for this application were: 1) The modes of transportation for oil and aniline are basically the same (pipes, barrels, tank cars). 2) The petroleum industry studies cited above predicted that approximately $7 \times 10^{-6}\%$ of the total product moved would be lost during transport and handling. 3) This loss was estimated to be divided 10% to air and 90% to water because of aniline's low vapor pressure, moderate solubility in water, and the likelihood that most spills would be cleaned up by hosing down the area before significant evaporation occurred. The amount of emissions released to air due to transport of exported aniline was: (2,800 kkg transported) x (7 x 10^{-8} kkg/kkg) x (0.10 fraction to air) = 2 x 10^{-5} kkg in 1978.

2.6.4.7.3 Emissions to Water

As described in section 2.6.4.7.2, transport of aniline was considered to be the only source of emissions during export. The amount of emissions was calculated as described in that section: (2800 kkg exported) x (7 x 10^{-8} kkg/kkg) x (0.90 fraction to water) = 2 x 10^{-4} kkg emissions to water during export in 1978.

TABLE 2.3 EMISSIONS DUE TO IMPORTS OF ANILINE (kkg)[1]

Year	Releases to Air During -		Releases to Water During -	
	Storage	Transport	Storage	Transport
1978	4×10^{-6}	7×10^{-9}		
1977	2×10^{-4}	4×10^{-7}		4×10^{-6}
1976				
1975	4×10^{-4}	7×10^{-7}		6×10^{-6}
1974	400×10^{-4}	600×10^{-7}		600×10^{-6}

[1] Calculation methods discussed in sections 2.5.2.1 and 2.5.2.2.

TABLE 2.5 ANILINE: CONSUMPTION BY ISOCYANATE MANUFACTURE[1]

Isocyanate Synthesis	% of Aniline Used Within Category	1978 (kkg)	1977 (kkg)	1976 (kkg)	1975 (kkg)	1974 (kkg)
Diphenylmethane-4,4-diisocyanate	60	89,000	79,000	61,000	47,000	58,000
Polymethylene Polyphenyl Isocyanate	40	59,000	53,000	40,000	31,000	39,000
TOTAL (Isocyanate Production)		148,000	132,000	101,000	78,000	97,000

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[1] A review of references (McCaleb, 1979; Hancock, 1975; Hahn, 1970; Kirk-Othmer, 1968; Simonds and Church, 1967) indicated that diphenylmethane-4, 4-diisocyanate used to be the dominant isocyanate; however, within the last five years polymethylene polyphenyl isocyanate has become commercially prominent. Therefore, it was estimated that diphenylmethane-4, 4-diisocyanate now only makes up 60 percent of the isocyanates manufactured from aniline. It was assumed that the manufactured amounts of these two isocyanates did not vary relative to each other over the five year period. Also, it was assumed that no other aniline-derived isocyanate had been manufactured on a commercial scale during this five year period.

TABLE 2.6 ANILINE: CONSUMPTION DURING PRODUCTION OF RUBBER CHEMICALS[1]

Rubber Chemicals	% of Aniline Used Within Category	1978 (kkg)	1977 (kkg)	1976 (kkg)	1975 (kkg)	1974 (kkg)
Accelerators	40	32,000	33,000	34,000	26,000	36,000
Antioxidants	30	24,000	25,000	25,000	20,000	27,000
Antiozonants	20	16,000	17,000	17,000	13,000	18,000
Curing Agents	10	8,000	8,000	8,000	7,000	9,000
TOTAL (Rubber Chemical Production)		80,000	83,000	84,000	65,000	90,000

[1] A review of the references (Hancock, 1975; Hahn, 1970; Lowenheim and Moran, 1975; Kirk-Othmer, 1968; Snell and Hilton, 1967) indicated that rubber accelerators make up the greatest percentage of the use of aniline as a single use in rubber chemicals industry. However, antidegradants, which is composed of antioxidants and antiozonants, appeared to have the greatest usage as a group of aniline in the manufacture of rubber chemicals. (Lowenheim and Moran, 1975; Kirk-Othmer, 1968.) The curing agents which are composed primarily of stabilizers, agents and retarders appeared to be produced in smaller quantities than antioxidants and antiozonants. (Lowenheim and Moran, 1975; Kirk-Othmer, 1968.) A review of aniline derivatives based on number, apparent quantities commercially manufactured, and uses also supported the estimated percent breakdown of aniline consumption in the rubber chemical industry (Hancock, 1975; Hahn, 1970; Lowenheim and Moran 1975; Kirk-Othmer, 1968; Snell and Hilton, 1967). No indication was obtained from the literature that would indicate a change in the percent of usage of aniline among the rubber chemicals or with changes in the total production of rubber chemicals over a five year period.

TABLE 2.7 ANILINE: CONSUMPTION BY THE CHEMICAL DYE CATEGORY[1]

Types of Dye Chemicals	% of Aniline Used Within Category	1978 (kkg)	1977 (kkg)	1976 (kkg)	1975 (kkg)	1974 (kkg)
Dyes & Intermediates						
Azoic	58	10,000	8,000	8,000	6,000	8,000
Indigoid	4	700	500	600	400	600
Stilbene	31	6,000	4,000	4,000	3,000	5,000
Triarylmethane	5	1,000	800	900	700	900
Pre Dye Fiber Treatment	1	200	1,000	100	100	100
TOTAL (Dye Chemicals Produced)		17,900	14,300	13,600	10,200	14,600

[1] Calculation of the aniline usage by Chemical Class and year was based upon Benzenoid Dye production (Hancock, 1975). The Chemical Classes were selected by using process descriptions from (EPA, 1977) and compilation of dyes mentioned in (Kirk-Othmer, 1968; Snell and Hilton, 1967; Hancock, 1975). The production of each of the four chemical types of dyes was totaled and a percent of the total for each type of dye was calculated. Based on a review of the references (TRW, 1973a; Hancock, 1975; Kirk-Othmer, 1968; TRW, 1973c; Snell and Hilton, 1967; EPA, 1977) it was felt that these percents reflect the aniline production percent usage in these chemical classes. Also based on the preceding references it was assumed that pre dye fiber treatment does not use more than one percent of the aniline production. It was assumed based on references (Hancock, 1975; Kirk-Othmer, 1968; Snell and Hilton, 1967; EPA, 1977) that percent usage of aniline per chemical dye class will not change drastically over the five year period 1974 to 1978.

TABLE 2.8 ANILINE: CONSUMPTION DURING THE PRODUCTION OF DRUGS[1,2]

Type of Drug Manufacture	% of Aniline Used By Category	1978 (kkg)	1977 (kkg)	1976 (kkg)	1975 (kkg)	1974 (kkg)
Sulfa Drugs	70	6,000	6,000	5,000	4,000	7,000
Antipyretic	14	1,000	1,000	1,000	800	1,000
Analgesic	14	1,000	1,000	1,000	800	1,000
Local Anesthetic	2	200	200	100	100	200
TOTAL Drug Manufacture		8,000	(8,000)[1]	7,000	6,000	10,000

[1] The 1977 miscellaneous category included drugs, hydroquinone, herbicides, fibers, and other compounds. This category used 34,000 kkg of aniline. The 1976 and 1978 figures were averaged to arrive at a realistic estimate for use of aniline in the Drug Manufacture.

[2] Determination of the quantity of aniline utilized in the production of drugs was arrived at by analyzing (USITC, 1976-1979; Kirk-Othmer, 1968; Snell and Hilton, 1967). Prior to the late 1960's antifebrin (acetanilide) was widely used as an antipyretic and analgesic hence representing the major usage of aniline in the drug industry. After the late 1960's antifebrin was replaced by another compound, hence reducing the aniline usage as an antipyretic and analgesic product (Snell and Hilton, 1967). During the late 1960's, the sulfa drugs became a dominant end product consumer of aniline in the drug industry. In the last five years it has maintained its dominant position while the anitpyretic and analgesic aniline based compounds have been relegated to secondary consumers of aniline. With the demise of the antipyretic and analgesic aniline compounds, aniline based local anesthetic compounds have become a minimal consumer of aniline (Kirk-Othmer, 1968).

TABLE 2.9 ANILINE: CONSUMPTION DURING PRODUCTION OF THE MISCELLANEOUS COMPONENTS[2,3]

Types of Miscellaneous Compounds	% of Aniline Used Within Category	1978 (kkg)	1977 (kkg)[1]	1976 (kkg)	1975 (kkg)	1974 (kkg)
Pesticides	30	8,000	4,000	6,000	5,000	7,000
Herbicides	30	8,000	4,000	6,000	5,000	7,000
Resins	15	4,000	2,000	3,000	3,000	3,000
Corrosion Inhibitors	10	3,000	1,000	2,000	2,000	2,000
Petroleum Additives	5	1,000	600	1,000	800	1,000
Other Uses	10	3,000	1,000	2,000	2,000	2,000
TOTAL Miscellaneous Production		27,000	13,000	22,000	17,000	22,000

[1] The miscellaneous category included drugs, hydroquinone, herbicides, fibers and other compounds. This category used 34,000 kkg of aniline. The annual aniline usage figures for 1976 and 1978 in the Drugs and hydroquinone product groups were averaged to determine the potential use of aniline in these product areas. These figures were subtracted from the 1977 reported miscellaneous aniline consumption category. The remaining quantity of aniline is the aniline consumed in the miscellaneous products grouping for 1977.

[2] The two dominant consumers in the miscellaneous category are Pesticides and Herbicides. (McCaleb, 1979; Lowenheim and Moran, 1975; Kirk-Othmer, 1968; Snell and Hilton, 1967). Based on the number of references that cited a particular usage and the significance attributed to that usage by each reference, the endproduct uses of aniline in the miscellaneous category were selected (McCaleb, 1979; Lowenheim and Moran, 1975; Kirk-Othmer, 1968; Snell and Hilton, 1967; Hancock, 1975).

[3] No definitive ordering of the endproducts was attainable in those uses cited under OTHER USES heading in the miscellaneous uses of aniline. These products include: catalysts, explosives, organic synthesis, rocket fuel, and synthetic sweetening agents.

TABLE 2.10 ANILINE: EMISSIONS GENERATED DURING PRODUCTION OF ISOCYANATES (kkg)

	1978		1977		1976		1975		1974	
	Emissions		Emissions		Emissions		Emissions		Emissions	
Isocyanate Synthesized	air	water	air	water	air	water	air	water	air	water
Diphenylmethane-4,4-diisocyanate	11	2200	10	2000	8	1500	6	1200	7	1400
Polymethylene polyphenyl diisocyanate	8	1500	7	1300	5	1000	4	800	5	1000
Total Emissions Per Year	19	3700	17	3300	13	2500	10	2000	12	2400

TABLE 2.11 ANILINE: EMISSIONS GENERATED DURING PRODUCTION OF RUBBER CHEMICALS (kkg)

Rubber Chemicals	1978 Emissions		1977 Emissions		1976 Emissions		1975 Emissions		1974 Emissions	
	air	water	air	water	air	water	air	water	air	water
Accelerators	8	1600	8	1600	9	1700	7	1300	9	1800
Antioxidants	6	1200	6	1200	6	1200	5	1000	7	1300
Antiozonants	4	700	4	800	4	800	3	600	5	900
Curing Agents	2	400	2	400	2	400	2	300	2	400
Total Loss Per Year	20	3900	20	4000	21	4100	17	3200	23	4400

TABLE 2.12 ANILINE: EMISSIONS GENERATED DURING PRODUCTION OF DYES AND INTERMEDIATES (kkg)

Dyes and Intermediates	1978 Emissions		1977 Emissions		1976 Emissions		1975 Emissions		1974 Emissions	
	air	water	air	water	air	water	air	water	air	water
Azoic	3	500	2	400	2	400	3	300	2	400
Indigoid	0	40	0	30	0	30	0	20	0	30
Stilbene	1	300	1	200	1	200	1	200	1	200
Triarylmethane	0	50	0	40	0	40	0	30	0	40
Pre Dye-Treatment	0	9	0	6	0	7	0	5	0	7
Total Loss Per Year	4	900	3	680	3	680	3	550	3	680

TABLE 2.13 ANILINE: EMISSIONS GENERATED DURING PRODUCTION OF HYDROQUINONE (kkg)

	Emissions	
Year	Air	Water
1978	4	700
1977	3	600
1976	3	600
1975	2	400
1974	4	700

TABLE 2.14 ANILINE: EMISSIONS GENERATED DURING DRUG MANUFACTURE (kkg)

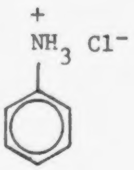
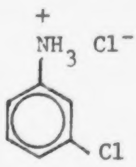
	Emissions	
Year	Air	Water
1978	0	85
1977	0	76
1976	0	67
1975	0	53
1974	0	92

TABLE 2.15 ANILINE: GENERATED EMISSIONS DURING MANUFACTURE OF THOSE COMPOUNDS IN THE MISCELLANEOUS CATEGORY

Miscellaneous Compounds	1978 Emissions		1977 Emissions		1976 Emissions		1975 Emissions		1974 Emissions	
	air	water	air	water	air	water	air	water	air	water
Pesticides	1	200	0.5	100	0.8	150	.9	170	0.6	120
Herbicides	1	200	0.5	100	0.8	150	.9	170	0.9	170
Resins	0.5	100	0.3	50	0.4	70	0.3	50	0.4	70
Corrosion Inhibitors	0.4	80	0.1	30	0.3	50	0.3	50	0.3	50
Petroleum Additives	0.1	20	0.05	10	0.1	25	0.1	25	0.1	25
Other Uses	0.4	80	0.1	30	0.3	50	0.3	50	0.3	50
Total Emissions Per Year	3.4	680	1.6	320	2.7	500	2.8	520	2.6	490

3.0 ANILINE HYDROCHLORIDE, m-CHLOROANILINE HYDROCHLORIDE

3.1 PHYSICAL PROPERTIES OF ANILINE HYDROCHLORIDE AND m-CHLOROANILINE HYDROCHLORIDE

Chemical Formula	$C_6H_7N \cdot HCl$	$C_6H_6ClN \cdot HCl$
Chemical Structure	 	
Molecular Weight	129.60	164.04
Melting Point	198°C	221.5°C
Boiling Point	245°C at 760 Torr	none available
Solubility	1,070 g/1 of H_2O	very soluble
Vapor Pressure	none available	none available
Density	1.22 g/cc	none available

The physical properties were abstracted from Stecher, 1968 and Weast, 1972.

Two physical properties of aniline hydrochloride aid in determining the environmental medium to which aniline hydrochloride may be released. The high solubility of aniline hydrochloride in water (1,070 g/1 of H_2O) suggests that much of the aniline hydrochloride lost during the manufacturing process and its application would probably be lost to the environmental water medium. If the vapor pressure were known for aniline hydrochloride, it would aid in estimating the quantity of aniline hydrochloride that could be released to the air during production and consumption.

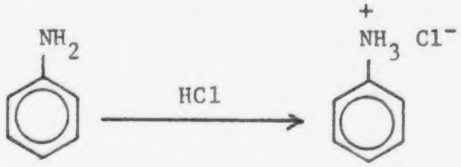
3.2 MATERIALS BALANCE FOR ANILINE HYDROCHLORIDE

Figure 3.1 shows the materials balance for aniline hydrochloride for the year 1978. The purpose of the following text is to explain the basis of our estimates and calculations that yielded the values reported in the figure.

3.3 DIRECT PRODUCTION OF ANILINE HYDROCHLORIDE

3.3.1 Production Processes, Producers and Locations

Aniline hydrochloride is produced by the direct reaction of aniline with hydrochloric acid. (Kirk-Othmer, 1968)



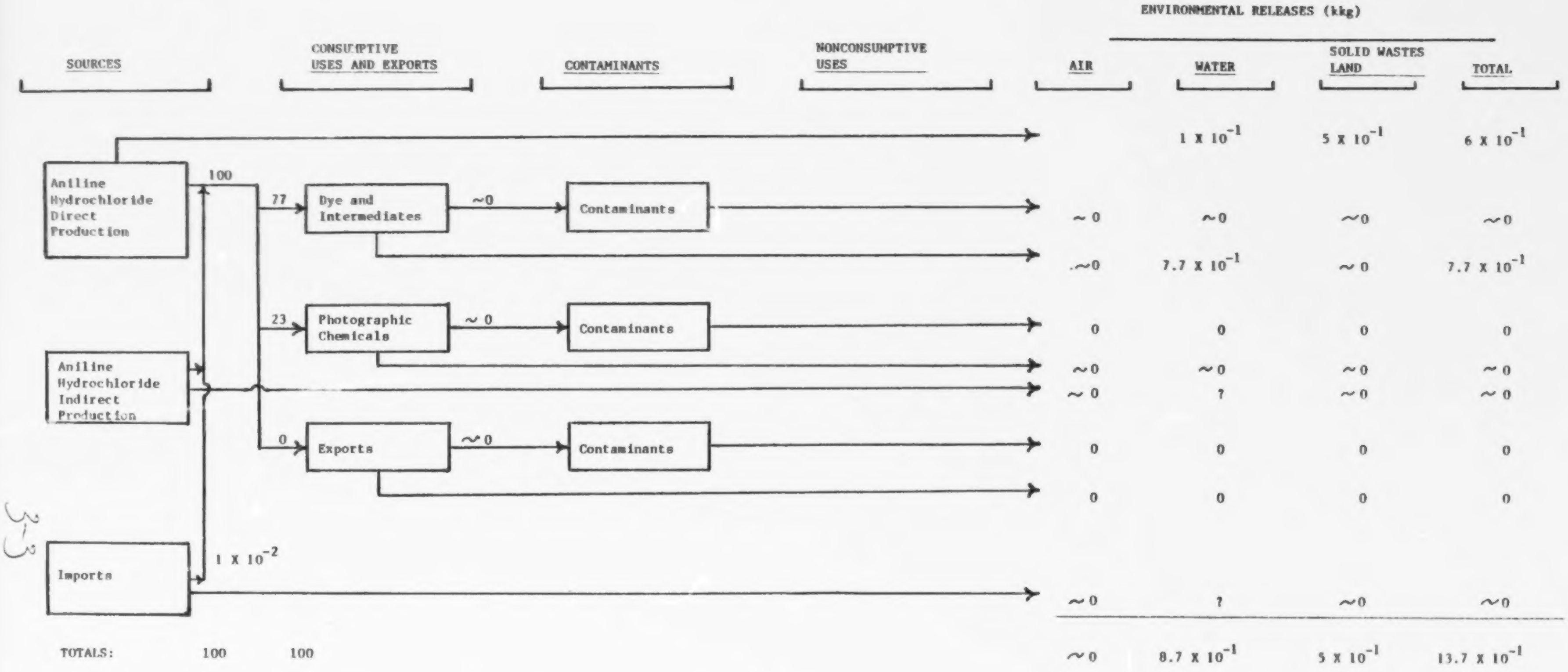
The literature cited two methods by which the direct reaction occurs: dry hydrogen chloride gas is passed through an ethereal solution of aniline; and concentrated hydrochloric acid is used to neutralize aniline which has been heated to 100°C with the mixture then being allowed to crystallize (Hawley, 1977).

The literature did not indicate which of the methods was the dominant one used in commercial production nor was there any discussion of the production process.

From discussions with American Cyanamid it was learned that their production process for aniline hydrochloride consisted of liquid aniline plus as aqueous solution of hydrochloric acid in the presence of a metallic catalyst (Personal Communication). The ratio of the reactants was not disclosed. Similar information about the production of aniline hydrochloride was not revealed by Tennessee Eastman Chemical.

USITC and EPA (1977) reported the following production information. The aniline hydrochloride report was confirmed by company spokesmen.

FIGURE 3.1 1978 MATERIALS BALANCE FOR ANILINE HYDROCHLORIDE (KKG)


ENVIRONMENTAL RELEASES (kkg)
SOURCES
CONSUMPTIVE USES AND EXPORTS
CONTAMINANTS
NONCONSUMPTIVE USES
AIR
WATER
SOLID WASTES LAND
TOTAL
Aniline Hydrochloride Direct Production
Aniline Hydrochloride Indirect Production
Imports
100
1 X 10^{-2}
77
23
0
Dye and Intermediates
Photographic Chemicals
Exports
~0
~0
~0
Contaminants
Contaminants
Contaminants
1 X 10^{-1}
5 X 10^{-1}
6 X 10^{-1}
~0
~0
~0
~0
.~0
7.7 X 10^{-1}
~0
7.7 X 10^{-1}
0
0
0
0
~0
~0
~0
~0
~0
?
~0
~0
0
0
0
0
0
0
0
0
~0
?
~0
~0
TOTALS:
100
100
~0
8.7 X 10^{-1}
5 X 10^{-1}
13.7 X 10^{-1}

Compound	Company	Location	Years Listed as Producer	Production (kkg)
aniline hydrochloride	American Cyanamid	Bound Brook, NJ	1974-1978	n.a.
	Tennessee Eastman Chem.	Kingsport, TN	1974-1978	n.a.
m-chloroaniline hydrochloride	Alliance Chem.	Newark, NJ	1977	0
	Blackman-Uhler Chem. Div.	Spartanburg, SC	1977	0.5-5

No other information on producers and locations was available.

3.3.2 Amounts of Aniline Hydrochloride Produced

No production or capacity figures were available in the references reviewed. Discussions with American Cyanamid and Tennessee Eastman Chemical suggested that the production of aniline hydrochloride was somewhere between 4.6 kkg and 100 kkg. The lower estimate was derived from the fact that companies are required to report to USITC when production exceeds 2.3 kkg or $5,000. Two companies reported production of aniline hydrochloride, indicating that at least 4.6 kkg of this were manufactured.

The higher value was selected based on discussions with American Cyanamid about the plant capacity at Bound Brook, New Jersey. The source indicated that the aniline hydrochloride capacity was considerably below the aniline plant capacity of 30,000 kkg, yet above 30 kkg. From this conversation it was determined that the production of aniline hydrochloride may be as high as 77 kkg.

Information was obtained on the production of aniline hydrochloride from Tennessee Eastman Chemical. The USITC reports from 1974 through 1978 indicate that Tennessee Eastman Chemical did not report the production of aniline. Since aniline hydrochloride was made from aniline, it would be more economical to manufacture large quantities of aniline and captively consume them in aniline hydrochloride production than to buy it from an outside source. Based on this reasoning, and discussions with a spokesman from Tennessee Eastman Chemical, it was estimated that the Eastman production of aniline hydrochloride constitutes a range from 2.3 kkg to 23 kkg. Thus, the total production of aniline hydrochloride was estimated to fall within the range 4.6-100 kkg/yr.

3.3.3 Emissions of Aniline Hydrochloride Due to Direct Production

Based on a conversation with American Cyanamid, it was learned that the only waste from the production of aniline hydrochloride is in the form of a liquid waste stream. A spokesperson for Tennessee Eastman Chemical stated that no liquid or solid residues were produced during manufacture. He also felt no emissions to air occurred during productions. These assertions should be tested when further data are available.

3.3.3.1 Air Emission

Personal communication with American Cyanamid revealed that there is probably no release of aniline hydrochloride to the air pathway during production. If the vapor pressure and more information about the production process machinery were available a numerical estimate might be calculated. We believe that releases of aniline hydrochoride to the air during production were minute.

3.3.3.2 Water Emissions

Conversations with American Cyanamid indicated that the manufacture of aniline hydrochloride does produce a liquid waste stream. No information as to the character, constituents, and quantity of the liquid wastestream was obtained. However, the waste stream was treated by a central treatment plant at the American Cyanamid, Bound Brook (NJ) plant. The central treatment plant consists of a primary, secondary-biological, and tertiary-activated carbon treatment facilities. The loss of aniline hydrochloride to the environmental water medium was probably very small at this plant due to the treatment facilities.

It was estimated that 0.1% of the total aniline hydrochloride was lost to the water pathway:

$$0.1\% \times 4.6 \text{ kkg}^{1} \text{ (low production parameter)} = 4.6 \times 10^{-3} \text{ kkg}$$

$$0.1\% \times 100 \text{ kkg}^{1} \text{ (high production parameter)} = 1 \times 10^{-1} \text{ kkg}$$

[1] The aniline hydrochloride production figures were derived in section 3.3.2.

3.3.3.3 Disposal of Solid Waste

An American Cyanamid source stated that no solid waste was created during the production of aniline hydrochloride. However, it is believed that some aniline hydrochloride would be found in the sludge of the first treatment process of the plant water treatment facility. Based on the primary treatment process which was probably some type of settling method, it was estimated that 0.5% of the annual aniline hydrochloride was lost to the water pathway.

0.5% x 4.6 kkg (low estimate of production) = 2.3 x 10^{-2} kkg

0.5% x 100 kkg (high estimate of production) = 5 x 10^{-1} kkg

The annual production values were derived in Section 3.3.2 of this report.

3.4 INDIRECT PRODUCTION OF ANILINE HYDROCHLORIDE

Aniline hydrochloride will be produced in the environment if the pH of the surrounding water is below aniline's pKa value. If chloride ions are present, then aniline hydrochloride would result. No estimates of the quantity of aniline hydrochloride formed in this way were possible because of the lack of data on pH and aniline concentration in environmental water samples. We estimated that very small quantities of aniline hydrochloride would be produced in this manner.

3.5 IMPORTS OF ANILINE HYDROCHLORIDE

3.5.1 Quantity Imported

The USITC report on Imports of Benzenoid Chemicals and Products for 1974 through 1978 did not cite any import data for aniline hydrochloride. These reports did indicate that less than 1 x 10^{-2} kkg of aniline hydrochloride could be imported and this figure would not be reported in the USITC reports. Secondly, those values used in the USITC reports were only taken from the major east and Gulf coast ports of entry. Therefore they represent a statistical coverage value, depending on the year, from 76 to 99 percent. It was estimated that the average annual imports of aniline hydrochloride during 1974 to 1978 was 1 x 10^{-2} kkg. This figure was determined by calculating the average statistical coverage value for "intermediates" and then multiplying the average times the maximum amount of chemical that was not reported.

84% [four year average of the USITC statistical coverage value] x 1 x 10^{-2} kkg [maximum amount of aniline hydrochloride that could be imported without appearing in the USITC reports]

1 x 10^{-2} kkg [estimated four year average annual aniline hydrochloride imports]

3.5.2 Emissions Due to Imports

The estimated quantities imported were very small; therefore the contribution of aniline hydrochloride to the environmental media would be exceedingly small.

3.6 CONSUMPTION AND USE OF ANILINE HYDROCHLORIDE

The literature reviewed suggested several commercial uses for aniline hydrochloride: synthesis of diphenylamine dyes, N-ethylaniline, diethylaniline, and 2,4,6-tribromoaniline (Hahn, 1970; Hancock, 1975; Hawley, 1977; Kirk-Othmer, 1975; Snell and Hilton, 1967).

An American Cyanamid official stated that all of the aniline hydrochloride produced at its Bound Brook (NJ) plant between 1974 through 1978 was used in the manufacture of dyes and related products. The source further stated that all of the alkyl anilines are manufactured from aniline rather than aniline hydrochloride for economic reasons.

The aniline hydrochloride produced at the Tennessee Eastman Chemical was a transitory product in a long series of steps to produce photographic chemicals. (Personal communication with Tennessee Eastman Chemical.)

Based on the economic premise that the alkyl anilines were manufactured from aniline, it was felt that almost all of the annual aniline hydrochloride was used to manufacture dyes and related products, and photographic chemicals.

The spokespersons for American Cyanamid and Tennessee Eastman stated that the demand for aniline hydrochloride has not changed significantly for the period 1974 through 1978.

3.6.1 Emissions of Aniline Hydrochloride Due to the Manufacture of Dye and Related Products

The amounts and types of constituents used to manufacture dyes are so varied among dye classes and within the same dye class that it was impossible to estimate releases to air and water. The calculations and estimates below represented very broad emissions figures of aniline hydrochloride to the environmental pathways. Discussions with an industry expert on dyes and dyestuffs revealed the manufacturing process for mono-azo dyestuffs. (Personal Communication.) This information provided the background information for the estimates on emissions.

To get the dye out of its manufacturing solution, the solution is heated and then sodium choride is added. The dye precipitates out of solution with sodium chloride as a contaminant in ppb. The dye precipitate is filtered and pressed to form a dye cake. The dye cake is air dried down to a three to four percent water content. This process suggests three points where emissions can occur:

1) After the dye was precipitated from the solution, the mother liquid was probably pretreated and then released to the municiple sewage system. Because of the high solubility of aniline hydrochloride in water it was conceivable that one percent of the annual production of aniline hydrochloride could enter the environmental water medium.

1% x 2.3 kkg (low estimated production) = 2.3 x 10^{-2} kkg

1% x 77 kkg (high estimated production) 7.7 x 10^{-1} kkg

The production estimates for aniline hydrochloride were calculated in section 3.3.2.

2) The quantity of aniline hydrochloride lost to the air pathway during drying was unknown, because the vapor presssure of aniline hydrochloride was not stated in the literature. However, we feel that it was probably insignificant.

3) The free aniline hydrochloride that may contaminate the dye was estimated to be insignificant. This premise was based on a discussion with an industrial dyestuff expert.

3.6.2 Emissions of Aniline Hydrochloride Due to the Manufacture of Photographic Chemicals

In the absence of process flow diagrams or data on emissions or emission factors, it was difficult to estimate the types and quantities of emissions.

It was estimated that insignificant emissions to air and water media occur during the manufacturing process. This was based on the following: 1) Aniline hydrochloride was a transitory compound in a long series of processes. 2) A spokesperson at Tennessee Eastman stated that there was no liquid wastes and probably no emissions to air during the use of aniline hydrochloride.

3.6.3 Summary of Aniline Hydrochloride Emissions Due to Its Uses

Table 3. 1 summaries the estimated emissions to air and water generated during the manufacture of products.

3.7 EMISSIONS DUE TO EXPORTS

An investigation conducted by the Foreign Trade Commision consisting of a search of the July 1978 invoices revealed no exports of any of the aniline compounds.

TABLE 3.1 ANILINE HYDROCHLORIDE: EMISSIONS GENERATED DURING CONSUMPTION

Product Manufactured from	1978 Emissions kkg		1977 Emissions kkg		1976 Emissions kkg		1975 Emissions kkg		1974 Emissions kkg	
	air	water	air	water	air	water	air	water	air	water
Dyes and Dye Intermediates[1,2]		7.7×10^{-1}		7.7×10^{-1}		7.7×10^{-1}		7.7×10^{-1}		7.7×10^{-1}
Photographic Chemicals										
TOTAL										

[1] The high estimated production value was used to calculate the losses in water. The formula used for the caluclations is derived in section 3.6.1.

[2] It was assumed that the production of aniline hydrochloride and dyes did not change over the time period.

4.0 ANILINE HYDROBROMIDE

No informantion and data were found either in the literature or contacts with industry which suggest that aniline hydrobromide was commercially manufactured or used to produce end products in the United States.

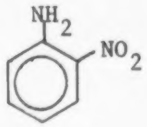
To ascertain if aniline hydrobromide was manufactured, a canvassing of the organic chemical industry must be undertaken.

In the absence of any data, we estimated that an insignificant quantity of aniline hydrobromide may be produced as a speciality chemical.

5.0 o-NITROANILINE

5.1 PHYSICAL PROPERTIES

The physical properties of o-nitroaniline are summarized below (Hawley, 1977; Weast, 1977-78; Strecher, 1968). Quantitative data on water solubility were not available; qualitative information is presented instead as a general guide.



o-nitroaniline
mol. wt. 138.12

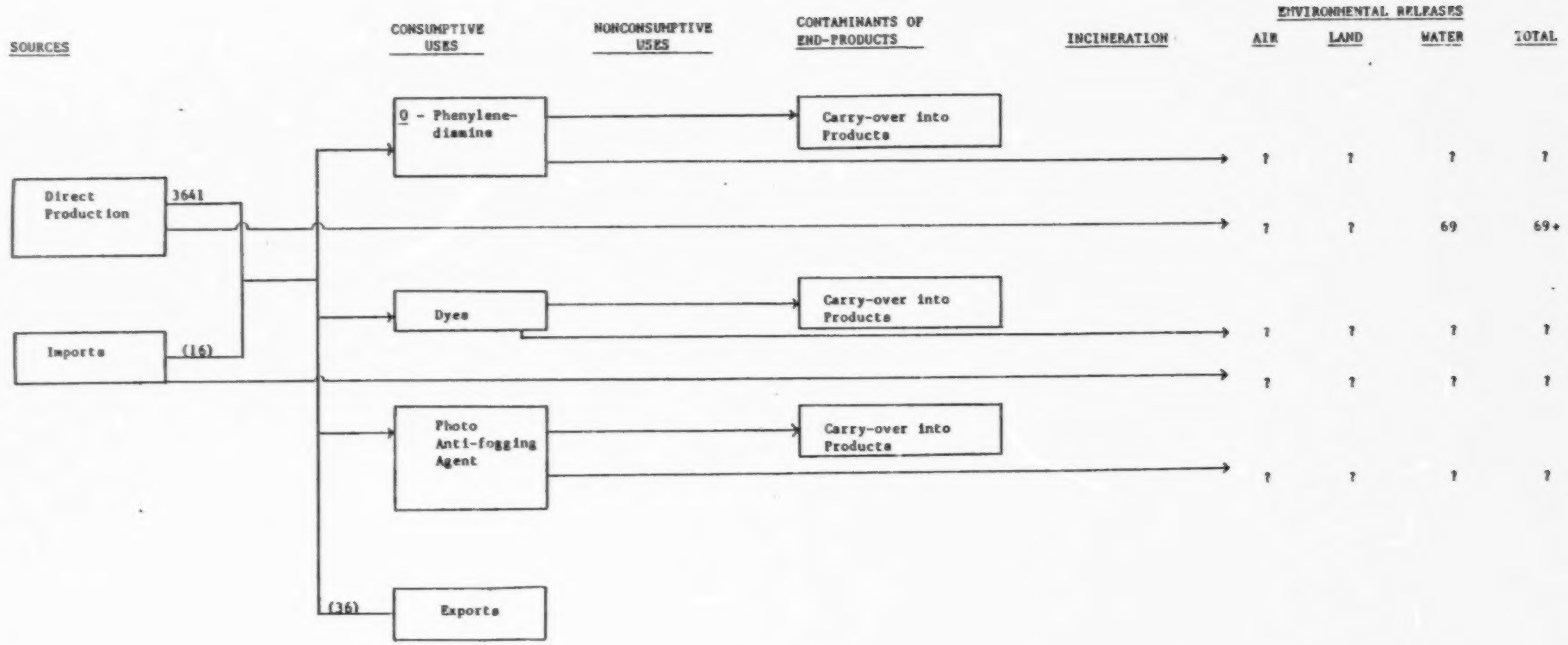
Melting point	71.5°C
Boiling point	284°C
Solubility in cold H_2O	slight
Solubility in boiling H_2O	soluble
Temp. at which vapor pressure = 1 Torr	104°C
pKa	

o-Nitroaniline is a solid at room temperature. It is characterized as soluble in hot water and has a vapor pressure lower than that of aniline (section 2.1).

5.2 MATERIALS BALANCE FOR o-NITROANILINE

Figure 5.1 shows the materials balance for o-nitroaniline. It points out the sources of o-nitroaniline (production, imports), the uses of the compound (consumption categories), and the estimated emissions to air, land, and water due to each process, when possible. This figure describes the most recent year for which data were available: 1978. The purpose of this chapter is to explain the assumptions and calculations that yielded the values reported in the materials balance.

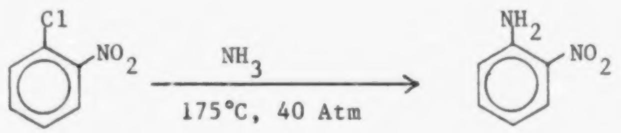
FIGURE 5.1 MATERIALS BALANCE FOR O - NITROANILINE (KKG)


SOURCES
CONSUMPTIVE USES
NONCONSUMPTIVE USES
CONTAMINANTS OF END-PRODUCTS
INCINERATION
ENVIRONMENTAL RELEASES
AIR
LAND
WATER
TOTAL
Direct Production
3641
Imports
(16)
O - Phenylene-diamine
Dyes
Photo Anti-fogging Agent
Exports
(36)
Carry-over into Products
Carry-over into Products
Carry-over into Products
? ? ? ?
? ? 69 69+
? ? ? ?
? ? ? ?
? ? ? ?

5.3 DIRECT PRODUCTION OF o-NITROANILINE

5.3.1 Production Process, Producers, and Locations

o-Nitroaniline was reported to be synthesized by high-pressure ammonolysis of o-chloronitrobenzene (Hancock, 1975):



5.3.2 Amounts Produced

Only Monsanto and duPont were listed as producers in 1978 (Catalytic, Inc., 1978). Producers in years previous to 1978 are listed in Table 5.1 (end of chapter). The amounts of o-nitroaniline produced in 1978 by duPont and Monsanto, respectively, are shown in Table 5.2. These results were reported in Catalytic, Inc., 1978, with no information on the method used to obtain them or an estimate of their accuracy.

TABLE 5.2 PRODUCTION OF o-NITROANILINE, 1978 (kkg)

Producer and Location	Reported Production	(% of total)
E. I. duPont de Nemours Deepwater, NJ	248	(7%)
Monsanto Chem. Co. Sauget, IL	3393	(93%)
SUM	3641	

The total production for 1978 was reported to be 3641 kkg, with Monsanto producing the vast majority of that amount.

5.3.3 Emissions Due to Production

5.3.3.1 Emission to Air

An industrial process flow chart was not available for the ammonolysis of o-chloronitrobenzene, nor were data on emissions or emission factors during production of o-nitroaniline. Therefore, it was not possible to reasonably estimate air emissions due to this process. To fill this data gap, the following information is needed: 1) air monitoring data, especially near the major production facility in Sauget, Illinois; 2) process information to permit pinpointing of emission sources; 3) information on waste treatment at Monsanto (incinerators, scrubbers, etc.).

5.3.3.2 Emissions to Water

Emissions to water can occur during synthesis (process water). Direct data were not available on o-nitroaniline emissions during this step. A best judgement estimate was made. 69 kkg o-nitroaniline were estimated to be released to water during production in 1978. This value was obtained by the operation: (kkg o-nitroaniline produced) x (emission factor, kkg/kkg) = kkg emission.

In the absence of data on emission factors, we estimated an emission factor for this process to be 1.9×10^{-2} kkg/kkg. This value was estimated using the following steps: 1) Fed. Reg. (1976) lists proposed rules for effluent limitations guidelines as limiting the 30-day average for o-nitroaniline to 27 kg COD/kkg product. 2) This effluent guideline measured in kg COD was converted to kg o-nitroaniline by assuming that (a) all of the COD was due to o-nitroaniline and (b) the o-nitroaniline was quantitatively oxidized to 6 CO_2 in the COD measurement. Therefore, 6 (32) = 192 g. (6 moles) of oxygen was equivalent to 138 g. (1 mole) of o-nitroaniline. The effluent limitation was expressed as $(27 \text{ kg COD/kkg product}) \times \left(\frac{138 \text{ kg product}}{192 \text{ kg oxygen demand}}\right) = 19$ kg o-nitroaniline released/kkg o-nitroaniline produced. 3) This value was considered to be the maximum emission factor for aqueous discharge of o-nitroaniline by assuming that production facilities obeyed the effluent guidelines. The emisssion factor was thus 0.019 kkg/kkg.

The uncertainty of this emission factor was estimated to be +50%, -90% based on the following: 1) It was an overestimate if (as seems likely) less than 100% of the COD was due to o-nitroaniline. 2) It was an underestimate if the chromic acid oxidation did not stoichiometrically degrade all of the o-nitroaniline in a COD measurement.

Application of this emission factor yielded: (3641 kkg produced) x (1.9 x 10^{-2} kkg/kkg) = 69 kkg o-nitroaniline generated for release to water during production in 1978.

5.3.3.3 Emissions Due to Disposal of Solid Residues

No direct data on emissions nor data on emission factors were available to permit estimation of emissions due to disposal of solid, o-nitroaniline-containing residues formed during production. In order to be able to estimate emissions to air, land, and water due to this disposal, the following information would be needed: 1) process engineering information on the sources of residues during the synthesis process; 2) quantitative analysis of residues produced; 3) rate of production of residues; 4) information on waste disposal methods at each plant (i.e., landfill, incineration, activated sludge treatment, stack gas scrubbers, etc.). Since o-nitroaniline is a solid and is only slightly water-soluble at room temperature, the chance of having solid o-nitroaniline residues is substantial.

5.4 INDIRECT PRODUCTION

Although opportunities for indirect production of o-nitroaniline undoubtedly exist, no information was available in this area.

5.5 IMPORTS OF o-NITROANILINE

5.5.1 Amounts

Table 5.3 shows available data on imports of o-nitroaniline for the past five years.

TABLE 5.3 IMPORTS OF o-NITROANILINE (kkg)[1]

1978	1977	1976	1975	1974
n.a.	n.a.	16	n.a.	91

[1] Source: USITC, Imports ofBenzenoid Chemicals and Products,
n.a. = not available

A datum was not available for 1978 imports, so the 1976 value was used in the Materials Balance (Figure 5.1).

5.5.2 Emissions Due to Imports

Data were not available on emissions due to transport and storage of imported o-nitroaniline. Furthermore, the oil spill/risk model described in section 2.5.2.1 was not considered applicable to a solid compound like o-nitroaniline. Therefore, estimates of emissions must await the availability of the following information: 1) more complete importation statistics; 2) monitoring data or a measured emission factor applicable to air, water, or total emissions.

5.6 CONSUMPTION AND USE

5.6.1 Categories of Use

o-Nitroaniline had two major industrial uses: 1) It was a starting reactant in the synthesis of o-phenylenediamine; and 2) It was used in the formation of dyes an dye intermediates. Table 5.4 (end of chapter) lists companies associated with each category. Of the two categories, o-phenylenediamine production was reported to be predominant (Hancock, 1975) but no percentage breakdown was given.

5.6.2 Amounts of Use

No data were available on amounts of o-nitroaniline consumed either in toto or by each of the major categories of use. Exports were estimated (McCaleb, 1979) to account for 1% of production, or 36 kkg in 1978. We had no criterion to evaluate the uncertainty of this value.

5.6.3 Emissions by Category of Use

Data on emissions during o-nitroaniline use were not readily available. In order to be able to report these emissions, one or more of the following would be needed: 1) Previously estimated emissions values from the literature; 2) Quantitative data on consumption of o-nitroaniline (total or by plant); 3) Process flow diagrams for consumption steps; 4) Measured effluent data on air and water waste streams at each consumption site; 5) Information on solid residue handling procedures at each consumption site; 6) Chemical analyses of solid residues containing o-nitroaniline; 7) Chemical analyses of products synthesized using o-nitroaniline.

TABLE 5.1 PRODUCERS OF *o*-NITROANILINE BY YEAR[1]

1978	1977	1976	1975	1974
duPont Deepwater, NJ	duPont	Synalloy Corp. Blackman-Uhler Chem. Div.	duPont	Monsanto
	Monsanto (450-4500 kkg)		Monsanto	
Monsanto Sauget, IL	X[2]	Monsanto		
	Salsbury Labs Leland, NC			
	GAF Corp. Rennselaer, NY (5-450 kkg)			
	Blackman-Uhler Chem. Div. Spartanburg, SC (5-450 kkg)			

[1] Sources: Catalytic, Inc., 1978; USITC, 1976-1978; EPA, 1977

[2] Manufacturer declined to be identified.

TABLE 5.4 INDUSTRIAL CONSUMPTION OF ORTHO-NITROANILINE

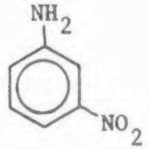
MANUFACTURING PROCESS	COMPANY [1]	PRODUCTS PRODUCED [2]
production of o-phenylene-diamine	E. I. du Pont de Nemours & Co., Inc. Sherwin Williams Co. Toms River Chemical Co.	dyestuffs pharmaceutical products rubber chemicals veterinary products
preparation of azo and anthroquinone dyes	Alliance Chemical Corp. American Color and Chemical Corp. GAF Corp., Chem. Division Synalloy Corp., Blackman-Uhler Chemical Div.	dyes and dye intermediates
		photo anitfogging agents

[1] USITC, 1976-79.

[2] TRW, 1973a; Hancock, 1975; Snell & Snell, 1962; Patty, 1963.

6.0 *meta*-NITROANILINE

6.1 PHYSICAL PROPERTIES OF *meta*-NITROANILINE

Chemical Formula	$C_6H_6N_2O_2$
Chemical Structure	
Molecular Weight	138.12
Melting Point	114°C
Boiling Point	306°C
Solubility	
Water	1.1 g/liter
Alcohol	50 g/liter
Ether	56 g/liter
Methanol	87 g/liter
Vapor Pressure	
Density	1.43 g/cc at 4°C

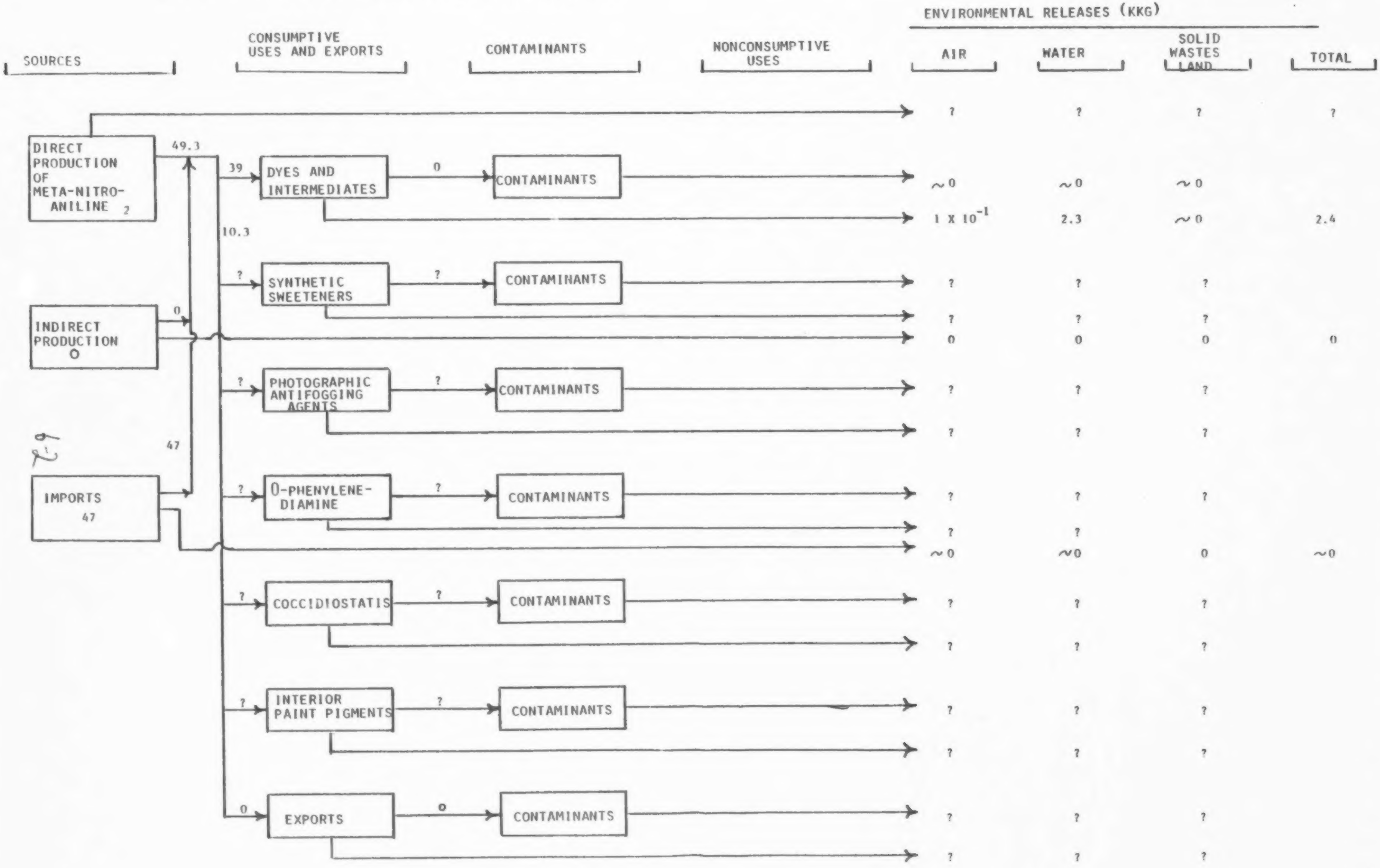
The physical properties were extracted from Stecher, 1968, and Weast, 1972.

Two physical properties of *m*-nitroaniline may be useful in estimating the quantity and medium by which *m*-nitroaniline may be released. The slight solubility of *m*-nitroaniline in water suggests that only small emissions could be accommodated dissolved in liquid wastestreams from manufacture and consumption. The low vapor pressure of *m*-nitroaniline suggest that spontaneous sublimation would be slow.

6.2 MATERIALS BALANCE FOR *meta*-NITROANILINE

Figure 6.1 shows the materials balance for *m*-nitroaniline for the year 1978. The following text explains the assumptions and calculations.

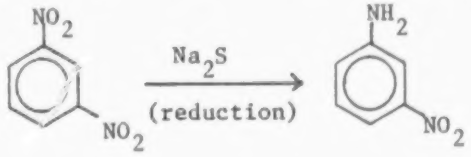
FIGURE 6.1 MATERIALS BALANCE FOR m-NITROANILINE (KKG)


ENVIRONMENTAL RELEASES (KKG)
SOURCES
CONSUMPTIVE USES AND EXPORTS
CONTAMINANTS
NONCONSUMPTIVE USES
AIR
WATER
SOLID WASTES LAND
TOTAL
DIRECT PRODUCTION OF META-NITRO-ANILINE 2
INDIRECT PRODUCTION O
IMPORTS 47
49.3
0
47
39
10.3
DYES AND INTERMEDIATES
SYNTHETIC SWEETENERS
PHOTOGRAPHIC ANTIFOGGING AGENTS
O-PHENYLENE-DIAMINE
COCCIDIOSTATIS
INTERIOR PAINT PIGMENTS
EXPORTS
CONTAMINANTS
?
~0
1 X 10^-1
2.3
2.4
0

6.3 DIRECT PRODUCTION OF meta-NITROANILINE

6.3.1 Production Process, Producers and Locations

The literature revealed three methods by which m-nitroaniline may be manufactured. E. G. Hancock stated that the normal production process was the partial reduction of m-dinitrobenzene with sulfides:



A second method of production was from m-nitrobenzoic acid, but the chemical steps were not available from the literature (Stecher, 1968). meta-Nitroaniline is produced from aniline by nitration after acetylation. The acetyl group is removed by hydrolysis yielding m-nitroaniline (Hawley, 1977). No mention was made in the literature as to the quantity of m-nitroaniline manufactured by the respective processes.

The USITC reports for 1974 through 1978 indicated that there was one producer of m-nitroaniline for 1974, 1976 and 1977. The producer was unknown because they requested not to be identified in the USITC reports. Further attempts at identifying the producer have been unsuccessful.

6.3.2 Quantity Produced

The amount of m-nitroaniline produced during the years 1974, 1976, and 1977 was not reported in the USITC due to its policy of not revealing production figures of an individual producer. However, the quantity produced during these years had to be greater than 2.3 kkg because companies are required to report production of products that exceed 2.3 kkg or $5,000.000.

The upper limit on the production of m-nitroaniline was difficult to estimate. Since only one company reported production, it was probably a small use commodity. Therefore, it was roughly estimated that no more than 45 kkg were produced.

Although production was not reported to the USITC during 1975 and 1978, this did not necessarily indicate that no m-nitroaniline was produced. It did suggest that from 0 kkg to 2.3 kkg was produced during these years.

6.3.3 Emissions Due to Direct Production

No information was available in the literature reviewed nor was it possible to create a production model on which emission estimates could be formulated.

6.4 INDIRECT PRODUCTION OF meta-NITROANILINE

No method of indirect production was stated or could be inferred from the references reviewed.

6.5 IMPORTS OF meta-NITROANILINE

6.5.1 Amounts Imported

Year	Statistical Coverage Value	Quantity kkg
1978	76%	47
1977	81%	15
1976	80%	95
1975	94%	48
1974	99%	86

These values were calculated based on the USITC Imports of Benzenoid Chemicals and Products for 1974 through 1978. Each of these reports contained a "statistical coverage value" which represented an estimate of the percentage of the imports that were actually reported. The values in the table have been corrected to represent the total imports. The calculation to arrive at the corrected value is shown below:

$$\text{Import compound at 100\% value} = \frac{\text{USITC imported quantity x 100\%}}{\text{USITC statistical coverage value in \%}}$$

The corrected import figures did not reflect imports due to air transportation (personal communication with U.S. Department of Commerce).

6.5.2 Emissions Due to Imports

The quantity of emissions to air, land, and water of *m*-nitroaniline was difficult to assess due to the dearth of information in the literature reviewed. Releases to air and water would occur during the storage and transportation of imported *m*-nitroaniline. These emissions would be due to spills and damaged containers. Losses to the water medium probably made up 80 percent of the loss and 20 percent was lost to the air medium. Spills were probably cleaned up by shoveling the chemical back into the container or hosing the area down.

Losses to the air were probably in the form of particulate matter. Air movements near spills would cause the crystals to become airborne. In the absence of any data on emissions during transportation an overall best-judgement indicated that the loss was insignificant. This was based on the premise the *m*-nitroaniline was shipped in metal 55 gallon drums requiring very little subsequent transfer or handling of contents.

6.6 CONSUMPTION AND USE OF *meta*-NITROANILINE

A review of the literature indicates that the prodominant use of *m*-nitroaniline was as a dye intermediate (Hancock, 1975; Hawley, 1977; Strecher, 1968; and TRW Systems Group, 1973). *m*-Nitroaniline has also been used to manufacture photographic antifogging agents, coccidostatics, interior paint pigments and synthetic sweeteners (Hawley, 1977; Kirk Othmer, 1968; Snell, 1963; and Snell and Hilton, 1964).

There are two areas to examine for *m*-nitroaniline emissions: 1) direct emissions during consumptive use and 2) carry-over as impurities in the manufactured products.

6.6.1 Total Consumption

Data were not available on the breakdown of the consumptive use of *m*-nitroaniline. Therefore, estimates of *m*-nitroaniline production were made based on the criteria used by USITC in reporting production and a general definition of what "small amounts" of production were to industry. These two limits were discussed in Section 6.3.2 of this report.

The major source of *m*-nitroaniline was imports.

The total *m*-nitroaniline available for consumption is presented in Table 6.1.

It was assumed that the *m*-nitroaniline produced and imported was consumed during that calendar year.

TABLE 6.1 INDUSTRIAL CONSUMPTION OF *meta*-NITROANILINE (kkg)

Year	Estimated Domestic Production Low	Estimated Domestic Production High	Imports	Total Low	Total High
1978	0	2.3	47	47	49.3
1977	2.3	45	15	17.3	60
1976	0	2.3	95	95	97.3
1975	2.3	45	48	50.3	93
1974	2.3	45	86	47.3	131

6.6.2 Emissions Due to Dye Manufacture

The predominant consumer of *m*-nitroaniline was probably the manufacture of dyes. The basis for this assumption was the literature reviewed. Several references cited the manufacture of dyes as the only use of *m*-nitroaniline

(Hancock, 1975; Patty, 1963; Snell, Snell, 1962; and Stecher, 1968). In the absence of any data on the consumption by the different endproducts, our best estimate was that 80 percent of the *m*-nitroaniline was used in dye manufacture. The remaining 20 percent was used to manufacture all other products made from *m*-nitroaniline. In the absense of data on the amounts of emissions or emission factors, an overall best-judgement emission factor for emissions generated during dye synthesis was estimated. The value estimated was 5 x 10^{-2} kkg/kkg. This emission factor represented the sum of the air and water emisssions. It was based on the following considerations: 1) In any chemical synthesizing process, only the introduction and initial chemical reaction of *m*-nitroaniline was significant. 2) The average initial reaction would utilize 90% of the *m*-nitroaniline feedstock. 3) Of the remaining 10% of *m*-nitroaniline; 5% was reclaimed and recycled and the other 5% was lost to water and air media as emissions. Therefore, the emission factor for *m*-nitroaniline emissions generated during dye manufacture was calculated as follows: (0.10 fraction not used) x (0.50 fraction of unused not reclaimed) = 0.05 kkg generated/kkg m-nitroaniline consumed.

6.6.2.1 Generated Emissions to Air

Due to lack of data on air emissions or emission factors during dye manufacture, the estimated factor derived in the preceding section (5 x 10^{-1} kkg/kkg) was applied to estimate the generated emissions to air during dye manufacture. To determine the emissions to air, it was estimated that 95% of emissions of *m*-nitroaniline were through the water medium and 5% of the air medium. The loss to air would be in the form of particulate matter. The loss would primarily occur during the emptying of the drums containing the crystals of *m*-nitroaniline into the dye manufacturing vessel. The calculations for emissions to air are presented below:

(49 kkg *m*-nitroaniline, high estimate use) x (5 x 10^{-2} kkg/kkg used) x (0.5 fraction to air) = 1.1 x 10^{-1} kkg generated for release to air during dye production in 1978.

The calcualted emission to air did not change significantly when the low estimate of *m*-nitroaniline usage for 1978 was used.

No data were available on the make up of the 20% of m-nitroaniline production that was not used in dye manufacture. Therefore, no attempts at estimating the emissions of m-nitroaniline to the air, land and water media were made.

In order to estimate emissions accurately the following data would be necessary: 1) The percent of the total m-nitroaniline annual production consumed by each product. 2) Diagrams of the manufacturing processes with explanation on how these processes work and sources of emissions within the process. 3) The types, quantities, and compositions of wastes from the manufacturing processes. 4) The waste treatment facilities at each plant and their efficiencies. 5) The final disposition of the wastes.

6.6.2.2 Generated Emissions to Water

The approach to estimating emissions generated during dye manufacture was described in Section 6.6.2.1 (above). The only value which changed in the calculation was the percent loss: From 5% air to 95% water. The emissions to the water medium were calculated as follows:

(49.3 kkg m-nitroaniline, high estimate) x (5 x 10^{-2} kkg/kkg consumed) x (0.95 fraction to water) = 2.3 kkg generated for release to water during dye production in 1978.

6.6.2.3 Emissions Due to Disposal of Solid Wastes

No data nor emissions factors were available to permit an estimate of emissions due to solid, m-nitroaniline-containing residues formed during dye synthesis. For an accurate estimate of emissions to air, land and water media as a result of this disposal, the following would be needed: 1) Process engineering information on the sources of residues during each process utilizing m-nitroaniline; 2) Information on the present contributions of the individual processes to the total for that dye class: 3) Quantitative analysis of residues produced; quantities of residue produced; 4) The waste treatment facilities and their efficiency; 5) The disposition of the solid residue (landfill, incineration, etc.).

6.6.3 Emissions Due to Manufacture of Other Products from m-Nitroaniline

The consumption of m-nitroaniline for manufacture of other products was estimated to be 20% of annual production. Refer to Section 6.6.2 of this report for the basis of this estimate.

Other products manufactured from m-nitroaniline included: photographic antifogging agents; o-phenylenediamine; coccidiostatics; interior paint pigments; and synthetic sweeteners (Hawley, 1977, Kirk-Othmer, 1968; and Snell-Hilton, 1967).

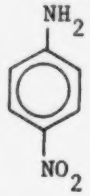
6.7 EMISSIONS DUE TO EXPORTS OF meta-NITROANILINE

An investigation conducted by the Foreign Trade Commission consisting of a search of the July 1978 invoices revealed no exports of m-nitroaniline.

7.0 *para*-NITROANILINE

7.1 PHYSICAL PROPERTIES OF *para*-NITROANILINE

para-Nitroaniline is also known as *para*-nitraniline and 1-amino-4-nitrobenzene. It is a fine needle yellow powder at room temperature. (Hawley, 1977). Its physical properties are summarized below:

Chemical Structure	
Chemical Formula	$NO_2C_6H_4NH_2$
Molecular Weight	138.13
Melting Point	146°C
Boiling Point	332°C
Solubility in:	
cold H_2O	0.8 g/1
warm H_2O	22 g/1
alcohol	40 g/1
ether	33 g/1
Density	1.424 g/cc at 4°C
Temp at which vapor pressure = 1 Torr	142.4°C

The physical properties that were of particular value in estimating emissions were the solubility in cold water and the vapor pressure.

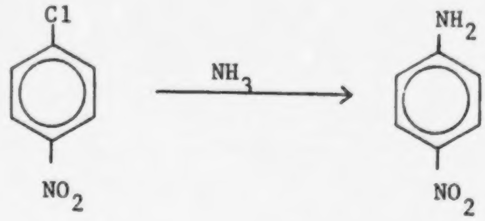
7.2 MATERIALS BALANCE FOR para-NITROANILINE

Figure 7.1 depicts the materials balance for p-nitroaniline for the year 1978. It shows the sources of p-nitroaniline (production and imports), the consumptive uses and exports, and the estimated emissions to air, water, and land due to each process.

7.3 DIRECT PRODUCTION OF para-NITROANILINE

7.3.1 Production Processes, Producers, and Locations

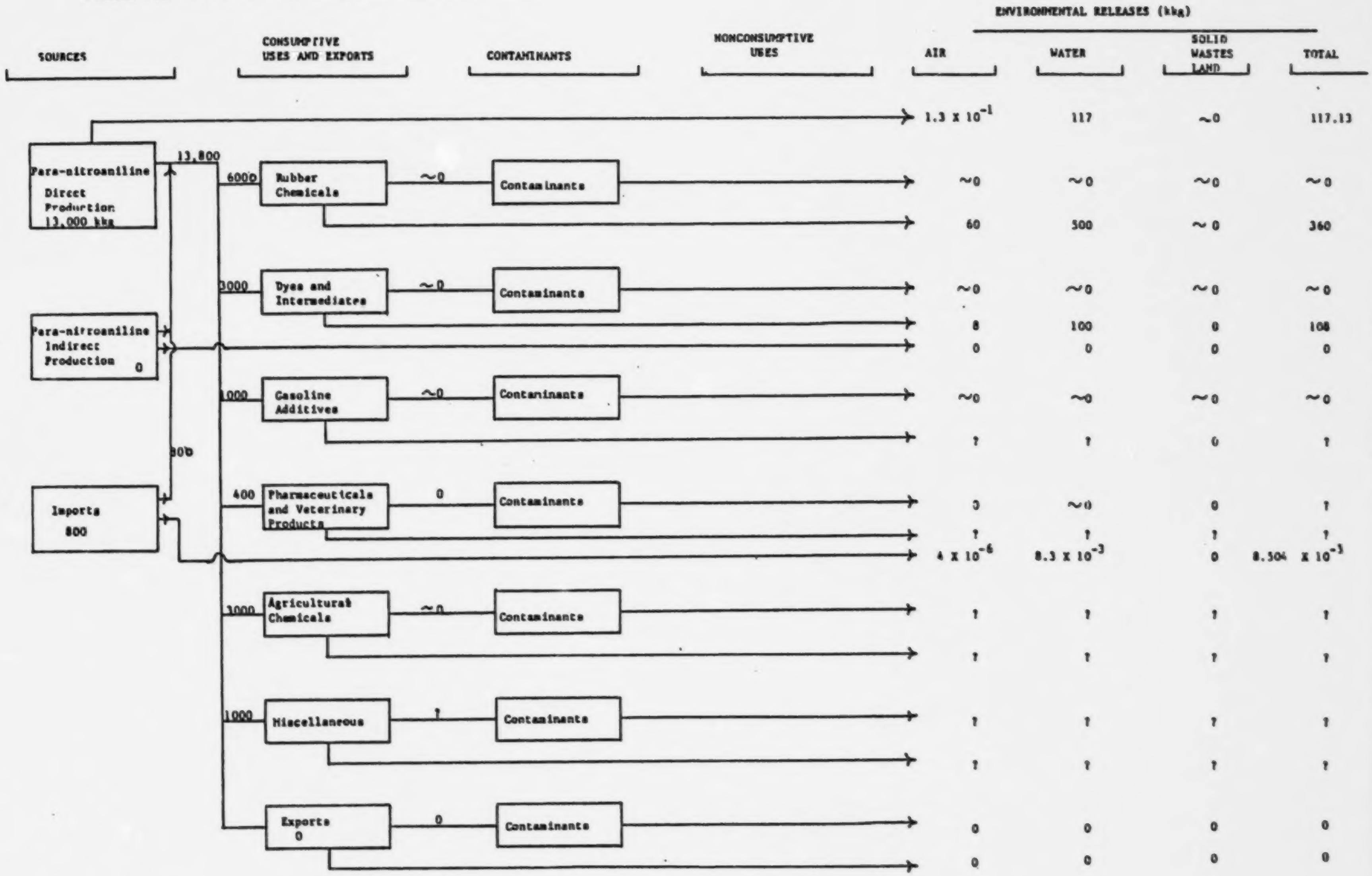
Literature indicated five methods for the synthesis of p-nitroaniline. E. G. Hancock (1975) stated that it was manufactured under pressure by the ammonolysis of p-chloronitrobenzene. The production process may be either batch or continuous (Hahn, 1970, Hawley, 1977 and Snell-Hilton, 1967).



An alternate procedure was by the nitration of acetanilide followed by hydrolysis (Hancock, 1975; Snell and Hilton, 1967; and Stecher, 1968).

The other three methods were: 1) nitration of aniline and then acetylation; 2) reaction of p-dinitrobenzene with alcoholic ammonia; and 3) acid-catalyzed addition of hydrazoic acid to carboxylic acids (Hawley, 1977; Snell, Snell, 1962; and Stecher, 1968). These methods were probably not used to any great extent in the commercial synthesis of p-nitroaniline. The first method mentioned (ammonolysis) was estimated to produce 80 percent and the second method (nitration) 20 percent of the annual domestic p-nitroaniline production.

FIGURE 7.1 MATERIALS BALANCE FOR p-NITROANILINE (KKG)


ENVIRONMENTAL RELEASES (kkg)
SOURCES
CONSUMPTIVE USES AND EXPORTS
CONTAMINANTS
NONCONSUMPTIVE USES
AIR
WATER
SOLID WASTES LAND
TOTAL
Para-nitroaniline Direct Production 13,000 kkg
Para-nitroaniline Indirect Production 0
Imports 800
13,800
800
6000
Rubber Chemicals
3000
Dyes and Intermediates
1000
Gasoline Additives
400
Pharmaceuticals and Veterinary Products
3000
Agricultural Chemicals
1000
Miscellaneous
Exports 0
~0
~0
~0
0
~0
?
0
Contaminants
1.3 X 10^-1 117 ~0 117.13
~0 ~0 ~0 ~0
60 300 ~0 360
~0 ~0 ~0 ~0
8 100 0 108
0 0 0 0
~0 ~0 ~0 ~0
? ? 0 ?
0 ~0 0 ?
? ? ? ?
4 X 10^-6 8.3 X 10^-3 0 8.304 X 10^-3
? ? ? ?
? ? ? ?
? ? ? ?
? ? ? ?
0 0 0 0
0 0 0 0

7.3.2 Amounts Produced

Data on the production of p-nitroaniline were difficult to obtain. There were four producers of p-nitroaniline in 1978. The production for only two of these companines was reported, and it was 6534 kkg for 1978 (Table 7.1). No production figures were available for the other two. The actual production was probably about twice this value or 13,000 kkg. The two companies for which no production was available were estimated to be similar in size to those that did supply data. Therefore, the estimated value represented twice the known value.

Refer to Table 7.1 for a list of the producers, and quantities produced where known from 1974 to 1978.

TABLE 7.1 PRODUCERS OF para-NITROANILINE BY YEAR, INCLUDING PRODUCTION WHERE AVAILABLE[1]

Compound	1978	1977	1976	1975	1974
p-Nitroaniline	duPont Deepwater, NJ	duPont	Monsanto	American Color & Chemical	American Color & Chemical
	American Color & Chemical Lockhaven, PA 1825 kkg produced	Monsanto 4500-23,000 kkg		duPont	duPont
		Salsbury Labs Leland NC		Monsanto	Monsanto
	Monsanto Sauget, Il 4709 kkg produced	Process Div., UOP Inc. Shreveport, LA			
	Signal Companies Shreveport, La				

[1] The manufacturing process used was the ammonolysis of p-nitrochlorobenzene.

7.3.3 Emissions Due to Direct Production

The lack of data on production, processes, manufacturing flow diagrams, and emission data and factors prevented calculation of precise estimates. However, in an attempt to provide some guidance, rough estimates were calculated for air and water emissions.

7.3.3.1 Generated Emissions to Air

Emission figures of p-nitroaniline to air during production were the sum of emissions due to: production, product storage, and product transport. We estimated the amounts of emissions generated to air by the following equation: (estimated kkg produced, stored and transported) x (emission factor in percent of annual production) = kkg released due to production, storage or transport. The estimated emissions to air are calculated below: 13,000 kkg/yr x 1 x 10^{-5} = 1.3 x 10^{-1} kkg loss of p-nitroaniline for 1978. The loss might be in the form of particulate matter due to the small size of the p-nitroaniline crystals.

The emission factor of 1 x 10^{-3} percent represented our best estimate of the likely loss to the air by a powdery substance, during production, storage and transport in closed containers.

7.3.3.2 Generated Emissions to Water

Emission figures of p-nitroaniline to water during production, product storage, and product transport were not readily available. The primary loss was estimated to be due to the production liquid waste stream, with minor amounts occurring due to spillage and container damage.

The effluent limitation guidelines for p-nitroaniline were used to estimate the loss to water. The proposed effluent limitation for p-nitroaniline (30 day average) is 13 kg COD/kkg of product. (Environmental Protection Agency, Organic Chemicals Manufacturing Paint Source Category, 1976.) The COD value was converted to kg p-nitroaniline by making the following assumptions; 1) All of the COD was due to p-nitroaniline. 2) The p-nitroaniline was quantitatively oxidized to 6 CO_2 in the COD measurement. The resulting equivalence of oxygen was 6(32) = 192 g oxygen and 138 g of p-nitroaniline. With an effluent limitation of 9 kg p-nitroaniline/kkg product (0.9% release), the maximum allowable emission factor would be calculated as: (13,000 kkg annual production) x (9 kg/kkg release factor based on COD) = 117 kkg of p-nitroaniline lost to the water medium during production, storage and transport.

The uncertainties of the estimate were: 1) it would be an overestimate if less than 100% of the COD were due to *p*-nitroaniline; 2) it would be understated if the chromic acid oxidation did not completely degrade all of the nitroaniline during COD measurements; 3) it assumed compliance with the guidelines by producers. The emission figure's uncertainty was estimated at +50%, -90%.

The *p*-nitroaniline lost to the liquid waste stream of the manufacturing plant was probably treated by a central treatment facility. In the worst instance, it would be treated only by a gross filtering or settlement treatment procedure removing at most 40% of the chemical waste. The liquid waste stream would then be released to a municipal sewage system.

Table 7.2 summarizes the estimated emissions (calculated as described above) due to production for the years 1974-1978.

TABLE 7.2 EMISSIONS OF *p*-NITROANILINE DURING SYNTHESIS

	EMISSIONS (kkg)	
YEAR	AIR	WATER
1978	13.0×10^{-2}	117
1977	9.8×10^{-2}	85
1976	4.7×10^{-2}	42
1975	11.2×10^{-2}	101
1974	11.2×10^{-2}	101

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[1] The production estimates upon which the emissions estimates were based are tabulated and footnoted in Table 7.1.

7.3.3.3 Disposal of Solid Residue

The lack of available data and emission factors prevented estimates of solid residue disposal. The information needed for an estimate on solid waste disposal would be: the quantity, type, and character of wastes generated during manufacture and waste treatment, and the methods used by each p-nitroaniline-producing plant.

7.4 INDIRECT PRODUCTION OF para-NITROANILINE

Analysis of the accessible literature and chemical synthesis possibilities did not indicate any indirect production method.

7.5 IMPORTS OF para-NITROANILINE

7.5.1 Amounts of para-Nitroaniline Imported

YEAR	STATISTICAL COVERAGE VALUE	QUANTITY, kkg
1978	76%	795
1977	81%	1620
1976	80%	984
1975	94%	1310
1974	99%	857

USITC Imports of Benzenoid Chemicals and Products for 1974 through 1978 was the source used to calculate the values above. By applying the statistical coverage value to the reported USITC value, the corrected import value was obtained.

$$\text{Import Compound at 100\% Value} = \frac{\text{USITC imported quantity} \times 100\%}{\text{USITC statistical coverage value in \%}}$$

The import values in the table above do not reflect air transported imports (Personal Communication with U.S. Department of Commerce).

7.5.2 Emission Due to Imports

Data on emissions and emission factors were not available for the determination of emissions to air, water and land media.

Emissions to air and water could occur during the storage and transportation of imported *p*-nitroaniline. These releases would be due to spills and leaks from damaged containers. Of the total loss, 80 percent was estimated to be lost to water and 20 percent lost to air. Spills would probably be cleaned up by shoveling the compound back into the container and hosing the area down. Emissions to the air would probably be in the form of particulate matter because *p*-nitroaniline is a crystalline solid.

p-Nitroaniline was probably imported in 55 gallon drums or similar container which would limit the amount of emissions. In the absence of any data on spills or container damage, it was estimated that the emissions from imports would be insignificant.

7.6 CONSUMPTION AND USE OF *p*-NITROANILINE

Current data on the consumption and uses of *p*-nitroaniline were not available. Therefore, the following assumptions are made, in an effort to provide estimates on quantities consumed by consumption categories: 1) In lieu of more recent figures, the consumption apportionment for 1969 was applied to 1974 through 1978 total *p*-nitroaniline domestic production and imports: rubber chemicals, 40%; dyes and intermediates, 20%; gasoline additives, 20%; pharmaceuticals and veterinary, 7%; agricultural chemicals, 3%; and miscellaneous, 10% (TRW Systems Group, 1973a). 2) There were no significant consumption changes among the product groups during this time period. 3) All of the *p*-nitroaniline produced and imported during a given calendar year was used during that year.

7.6.1 Total Consumption

Complete consumption and use figures were not available for the period 1974 through 1978. In order for estimates to be calculated, the following assumptions were necessary: 1) Consumption = production for the years under consideration. 2) The production of *p*-nitroaniline has remained constant from

1974 through 1978. 3) The Monsanto production for 1978 of 4709 kkg also represents the estimated amount produced by duPont. 4) The American Color and Chemical Company production for 1978 of 1825 kkg also represents the estimated amount produced by Signal Companies. The estimated domestic production for 1978 is 13,000 kkg + 795 kkg imports = 13,795 kkg the total available p-nitroaniline for consumption. Refer to Table 7.3 for consumption estimates 1974 through 1978.

7.6.2 Categories of Use

The categories of p-nitroaniline use, consuming companies, and amounts used for the past five years are presented in Table 7.4. The data were obtained from the footnoted references; we had no criterion on which to base an uncertainty estimate.

The rubber chemicals will probably increase the market share of p-nitroaniline, while dyes and dye intermediates and agricultural chemicals demand will steadily decrease. A detailed listing of the production processes, derivatives and uses are cited in Appendix B.

7.6.3 Emissions by Category of Use

7.6.3.1 Emissions Due to Rubber Chemicals

The estimate of emissions of p-nitroaniline from the production of rubber chemicals was based on the following assumptions: 1) para-Phenylenediamine was the feedstock for all the rubber chemicals. 2) The yield of p-phenylenediamine from p-nitroaniline was 90%. 3) para-Nitroaniline synthesis of para-phenylenediamine was a single step process. 4) para-Phenylenediamine contained no nitroaniline as impurity. 5) The 10% difference in actual and theoretical yield represented the p-nitroaniline lost to the environment. 6) Of the 10% lost to the environment, 90% was emitted to the water and 10% was emitted to the air. The emissions to air and water were calculated to be:

(6000 kkg, 1978 p-nitroaniline used to manufacture p-phenylenediamine) x (0.10 loss due to production of p-phenylenediamine) x (0.90 loss to the water) = 500 kkg lost to the water media during 1978. (6000 kkg, 1978 p-nitroaniline used to manufacture p-phenylenediamine) x (0.10 loss due to production of p-phenylenediamine) x (0.10 loss to air) = 60 kkg, lost to the air media during 1978.

TABLE 7.3 INDUSTRIAL CONSUMPTION OF PARA-NITROANILINE (kkg)

Year	Estimated Domestic Production	Imports	Total
1978	13,000[1]	795	13,795
1977	9,400[2]	1620	11,020
1976	4,700[3]	984	5,684
1975	11,000[4]	1310	12,310
1974	11,000[4]	857	11,857

[1] Calculations:

Producer	Quantity kkg
duPont	4709 (estimated)
Monsanto	4709
American Color and Chemical	1825
Signal Companies	1825 (estimated)
	13,068

[2] Calculations:

Producer	Quantity kkg
duPont	4709 (estimated)
Monsanto	4709
	9418

[3] Calculations:

Producer	Quantity kkg
Monsanto	4709

[4] Calculations

Producer	Quantity kkg
American Color and Chemical	1825
duPont	4709 (estimated)
Monsanto	4709
	11,243

TABLE 7.4 CATEGORIES AND AMOUNTS OF *para*-NITROANILINE CONSUMPTION

1974-1978 (kkg/year)

Manufacturing Process	% of Para-Nitroaniline Consumed	Company[1]	Products Produced	Year	Amount Used
Several Different Compounds	40	(No Users Cited)	rubber chemicals	1978	6000
				1977	4000
				1976	2000
				1975	5000
				1974	5000
Several Different Compounds	20	Allied Chemical Corp. American Color & Chemical Corp. Atlantic Chemical Corp. E.I. duPont de Nemours & Co., Inc. Fabricolor Manufacturing Corp. GAF Corp. Harshaw Chemical Co., Div. of Kewanee Oil Co. Mobay Chemical Corp. Southern Dyestuff Co.	dyes and dye intermediates	1978	3000
				1977	2000
				1976	1000
				1975	3000
				1974	2000

TABLE 7.4 CATEGORIES AND AMOUNTS OF *para*-NITROANILINE CONSUMPTION

(continued)

Manufacturing Process	% of Para-Nitroaniline Consumed	Company[1]	Products Produced	Year	Amount Used
Several Different Compounds	20	(No Users Cited)	agricultural chemicals	1978	3000
				1977	2000
				1976	1000
				1975	3000
				1974	2000
Several Different Compounds	7	(No Users Cited)	gasoline additives	1978	1000
				1977	1000
				1976	400
				1975	1000
				1974	1000
Several Different Compounds	3	(No Users Cited)	pharmaceuticals and veterinary products	1978	400
				1977	300
				1976	200
				1975	400
				1974	400

TABLE 7.4 CATEGORIES AND AMOUNTS OF *para*-NITROANILINE CONSUMPTION

(continued)

Manufacturing Process	% of *Para*-Nitroaniline Consumed	Company[1]	Products Produced	Year	Amount Used
Several Different Compounds	10	(No Users Cited)	miscellaneous	1978	1000
				1977	1000
				1976	600
				1975	1000
				1974	1000

[1] Sources: USITC, 1976-79; TRW, 1973a.

The 500 kkg was considered generated emissions instead of actual emissions, because the aqueous waste stream would be at least primary-treated before release to environmental waters.

The quantity of solid waste generated from the manufacture of rubber chemicals was unknown.

Accurate estimates of emissions can be calculated only with the following knowledge: 1) production processes and descriptions of the processes for each product; 2) emissions data or factors from manufacturing plants; 3) accurate production figures; 4) the types, character, and amounts of waste streams generated; 5) the types, efficiency and final disposition of waste treatment.

7.6.3.2 Emissions Due to Dyes and Dye Intermediates

Data were not available on air and water emissions or emission factors during dye synthesis. Estimates were calculated based on the following considerations: 1) The step that introduces p-nitroaniline into the multi-step process was the only step considered. 2) The yield was 90%, based on general engineering and economic considerations. 3) Of the remaining 10% of p-nitroaniline, 5% was reclaimed and recycled and the other 5% was lost to water and air media as emissions. Therefore, the emissions factor for p-nitroaniline emissions generated during dye manufacturing was calculated as follows: (0.10 fraction not used) x (0.05 fraction of unused not reclaimed) = 0.05 kkg generated/kkg p-nitroaniline consumed.

7.6.3.2.1 Generated Emissions to Air

In the absence of data on air emissions or emission factors during dye manufacture, the emission factor derived in the preceding section (5×10^{-2} kkg) was applied to determine the emissions to air during dye manufacture. It was estimated that 95% of the emissions of p-nitroaniline were to the water medium and 5% to the air medium. The loss to air would be mostly in the form of particulate matter and would occur during the emptying of drums into the dye reaction vessel. The calculations for emissions to air are presented below:

> (3000 kkg p-nitroaniline used to make dyes) x (5×10^{-2} kkg/kkg used) x (.05 fraction to air) = 8 kkg generated for release to air during dye production in 1978.

7.6.3.2.2 Generated Emissions to Water

The approach to estimating emissions generated during dye manufacture was described in section 7.6.3.2.1 (above). The only value which changed in the calculation was the percent loss to water: 95%. The emissions to the water medium were calculated as follows: (3000 kkg p-nitroaniline) x (5 x 10^{-2} kkg/kkg consumed) x (0.95 fraction to water) = 100 kkg generated for release to water during dye production in 1978.

7.6.3.2.3 Emissions Due to Disposal of Solid Wastes

No data nor emissions factors were available to permit an estimate of emissions due to solid, p-nitroaniline containing residues formed during dye synthesis. For an accurate estimate of emissions to air, land and water media as a result of this disposal, the following is needed: 1) Process engineering information on the sources of residues during each process utilizing m-nitroaniline; 2) Information on the percent contributions of the individual processes to the total for that dye class; 3) Quantitative analysis of residues produced; quantities of residue produced; 4) The waste treatment facilities and their efficiency; 5) The disposition of the solid residue (landfill, incineration, etc.).

7.6.3.3 Emissions Due to Agricultural Chemicals

No data on emissions or emission factors were readily obtainable. Refer to section 7.6.3.7 for further remarks.

7.6.3.4 Emissions Due to Gasoline Additives

No data on emissions or emission factors were readily obtainable. Refer to section 7.6.3.7 for further remarks.

7.6.3.5 Emissions Due to Pharmaceuticals and Veterinary Products

In the absence of data on emissions and emission factors no estimates were made. Refer to section 7.6.3.7 for further remarks.

7.6.3.6 Emissions Due to Miscellaneous Uses

In the absence of data on emissions and emission factors no estimates were made. Refer to section 7.6.3.7 for further remarks.

7.6.3.7 Summary of *p*-Nitroaniline Emissions

Refer to Table 7.5 for a summary of the emissions during manufacture of the products from *p*-nitroaniline.

Emissions for those products manufactured from *p*-nitroaniline could be calculated if the following data were available: 1) Consumption data on *p*-nitroaniline for each of the products. 2) The production flow diagram with explanation of each of the processes and product yields. 3) Data on the types, character, and quantity of waste streams. 4) The type and efficiency of the waste treatment facilities.

7.7 EMISSIONS DUE TO EXPORTS OF *para*-NITROANILINE

An investigation conducted by the Foreign Trade Commission consisting of a search of the July 1978 invoices revealed no exports of *p*-nitroaniline.

TABLE 7.5 *para*-NITROANILINE EMISSIONS GENERATED DURING ITS USE

Product Manufactured from *para*-nitroaniline by category	1978 Emissions kkg		1977 Emissions kkg		1976 Emissions kkg		1975 Emissions kkg		1974 Emissions kkg	
	air	water	air	water	air	water	air	water	air	water
Rubber Chemicals	60	500	40	400	20	200	50	500	50	400
Dyes and Dye Intermediates	8	100	6	100	3	50	6	100	6	100
Agricultural Chemicals										
Gasoline Additives										
Pharmaceuticals and Veterinary Products										
Miscellaneous										
TOTAL	68	600	46	500	23	250	56	600	56	500

8.0 OTHER NITROANILINES

This materials balance also reported readily available information on sixteen nitroanilines in addition to the three mononitroanilines considered separately in Chapters 5, 6, and 7. For the purposes of the present chapter, a nitroaniline was defined as any aniline containing a nitro group, whether or not a halogen was present in addition. The haloanilines are considered in Chapter 9.

8.1 PROPERTIES

Table 8.1 summarizes the physical properties of the nitroanilines being considered. Neither data on vapor pressures nor quantitative data on solubilities were available; qualitative characterizations of solubility are presented only as a general guideline. These compounds are solids at room temperature and exhibit almost no solubility in cold water.

8.2 MATERIALS BALANCE FOR NITROANILINES

In view of the lack of data available on the nitroanilines of interest here, neither individual nor a composite materials balance diagram was constructed.

8.3 PRODUCTION OF OTHER NITROANILINES

8.3.1 Producers and Locations

Figure 8.1 shows the locations and names of the producers of nitroanilines considered in this chapter. The producers are located in the eastern half of the country, mostly along the east coast and gulf coast.

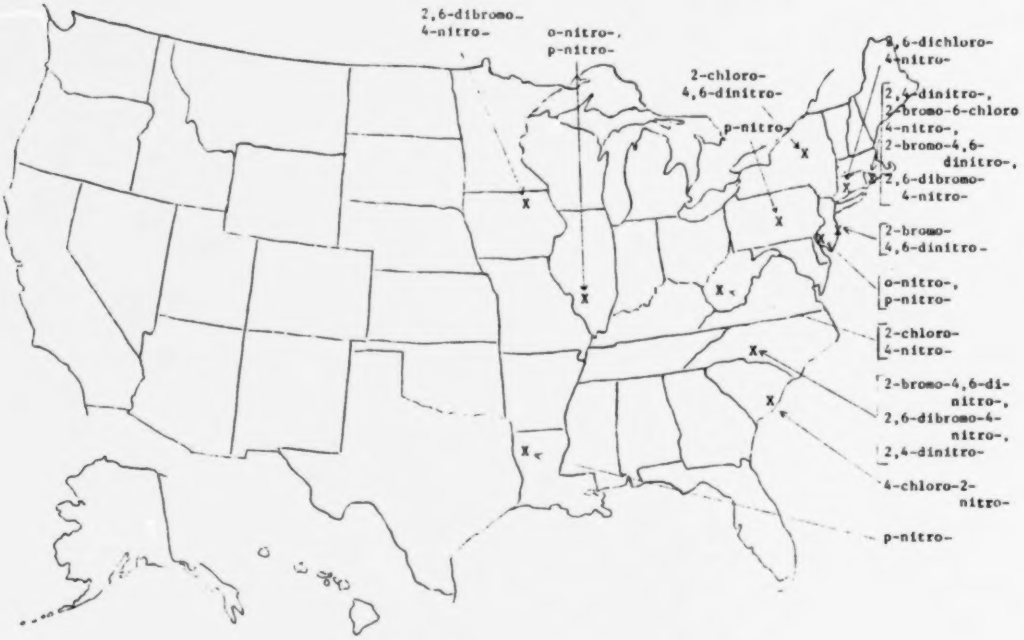
Table 8.2 (end of chapter) lists producers for the past five years. In 1974 and 1975, capacity figures were presented for three compounds, but not by individual producer. These total capacities figures are also presented in Table 8.2.

TABLE 8.1 PHYSICAL PROPERTIES OF NITROANILINES[1]

CLASS	COMPOUND	M.P.	B.P.	SOLUBILITY IN H_2O
Dinitroanilines	2,4-dinitro-	188°		insol
	2,6-dinitro-	141-142°		insol
Chloronitroanilines	4-chloro-2-nitro-	116.3°		insol
	2-chloro-4-nitro-	107°		slight
	4-chloro-3-nitro-	95-97°		partial
	2-chloro-6-nitro-	76°		
	3-chloro-4-nitro--	156-157°		
	5-chloro-2-nitro-	126.5°		
	3-chloro-5-nitro-	133-134°		
	2-chloro-5-nitro-	121°		
	4-chloro-2,6-dinitro-	147°		sol (hot)
	3-chloro-2,6-dinitro-	112°		sol (hot)
	2,6-dichloro-4-nitro-			
Bromonitroanilines	2,6-dibromo-4-nitro-	207°		slight
	2-bromo-4,6-dinitro-	153-154°		
Bromochloronitroaniline	2-bromo-6-chloro-4-nitro			

[1] Sources: Hawley, 1977; Weast, 1977-78.

FIGURE 8.1 LOCATIONS OF NITROANILINE PRODUCERS, 1978


2,6-dibromo-4-nitro-
o-nitro-, p-nitro-
2-chloro-4,6-dinitro-
p-nitro-
2,6-dichloro-4-nitro-
2,4-dinitro-, 2-bromo-6-chloro 4-nitro-, 2-bromo-4,6-dinitro-, 2,6-dibromo-4-nitro-
2-bromo-4,6-dinitro-
o-nitro-, p-nitro-
2-chloro-4-nitro-
2-bromo-4,6-dinitro-, 2,6-dibromo-4-nitro-, 2,4-dinitro-
4-chloro-2-nitro-
p-nitro-
X

LIST OF PRODUCERS

COMPOUND	PRODUCER	LOCATION
2,4-dinitroaniline	American Hoechst	Coventry, RI
	Martin-Marietta	Sodyeco, NC
2,6-dibromo-4-nitroaniline	American Hoechst	Coventry, RI
	Martin-Marietta	Sodyeco, NC
	Salsbury Labs	Charles City, IA
2,6-dichloro-4-nitroaniline	Upjohn Company	North Haven, CT
2-chloro-4,6-dinitroaniline	BASF Wyandotte	Rensselaer, NY
2-chloro-4-nitroaniline	Allegheny Ludlam Industries	Huntington, WV
4-chloro-2-nitroaniline	Mobay Corporation	Bushy Park, SC
2-bromo-6-chloro-4-nitroaniline	American Hoechst	Coventry, RI
2-bromo-4,6-dinitroaniline	American Hoechst	Coventry, RI
	Martin-Marietta	Sodyeco, NC
	Toms River Chemical Company	Toms River, NJ

8.3.2 Amounts Produced

Data were not available on current production of any of the nitroanilines considered here. These data are needed for any useful calculation of emissions due to production.

8.4 IMPORTS OF NITROANILINES

8.4.1 Amounts

Table 8.3 shows the data available on imports of nitroanilines. It was not known what fraction of domestic production these values represent.

8.4.2 Emissions Due to Imports

Data were not available on either emission amounts or emission factors attributable to nitroaniline imports. Furthermore, the oil spill/risk model described in Section 2.5.2.1 was not considered applicable to solid compounds like nitroanilines. Therefore, estimates of emissions must await the availability of the following information: 1) more complete importation statistics; 2) monitoring data or a measured emission factor applicable to air, water, or total emissions.

8.5 CONSUMPTION AND USE

No quantitative data were available on consumption processes for nitroanilines. This would appear to be an important area for future study.

TABLE 8.2 PRODUCERS OF NITROANILINES, 1974-1978[1]

Compound	1978	1977	1976	1975	1974
2,4-dinitroaniline	American Hoechst Coventry, RI	American Hoechst Coventry, RI			Amer. Color and Chem.
	Martin-Marietta Sodyeco, NC	Martin-Marietta Sodyeco, NC			Amer. Hoechst
		Chemtronics, Inc. Swannanoa, NC (< 0.5 kkg)			Martin-Marietta
					Toms River Chem Co. Toms River, NJ
					Total Capacities = 262 kkg/yr
2,6-dibromo-4-nitroaniline	American Hoechst	American Hoechst		American Hoechst	
	Martin-Marietta	Martin-Marietta		Martin-Marietta	
	Salsbury Labs Charles City, IA	Salsbury Labs		Salsbury Labs	
				Total Capacities = 20 kkg/yr	
2,6-dichloro-4-nitroaniline	Upjohn Co. North Haven, CT	Upjohn Co.		Upjohn Co.	
		Carroll Prod. Wood River Jct., RI			
		Drake Chem. Lockhaven, PA			
2-chloro-4,6-dinitroaniline	BASF Wyandotte Rensselaer, NY				

TABLE 8.2 PRODUCERS OF NITROANILINES, 1974-1978[1] (continued)

Compound	1978	1977	1976	1975	1974
2-chloro-4-nitroaniline	Allegheny Ludlam Industries Huntington, WV	duPont Co. Deepwater, NJ		duPont Co.	duPont Co.
4-chloro-2-nitroaniline	Mobay Corp. Bushy Park, SC	Amer. Cyanamid Bound Brook, NJ (5-45 kkg) G.F. Smith Chem. Columbus, OH duPont Co. (45-450 kkg) Carroll Prod.		duPont Co.	duPont
2-bromo-6-chloro-4-nitroaniline	American Hoechst			American Hoechst duPont	American Color and Chem.
2-bromo-4,6-dinitroaniline	American Hoechst Martin-Marietta Toms River Chem. Co.	American Hoechst Martin-Marietta Toms River Chem. Co. GAF Corp. Rensselaer, NY ICI Americas Dighton, MA	American Color and Chem. American Hoechst Martin-Marietta	Amer. Color and Chem. American Hoechst Martin-Marietta Toms River Chem. Co.	Amer Color and Chem. American Hoechst Martin-Marietta Toms River Chem Co. Total Capacities = 932 kkg/yr

TABLE 8.2 PRODUCERS OF NITROANILINES, 1974-1978[1] (continued)

Compound	1978	1977	1976	1975	1974
4-chloro-3-nitroaniline		Tennessee Eastman Kingsport, TN (45-450 kkg)			
4-chloro-2,6-dinitroaniline		Kodak Park Div. Rochester, NY			
2-chloro-5-nitroaniline		Tennessee Eastman Kingsport, TN (45-450 kkg)			

1. Source: USITC, 1976-1979; EPA, 1977

TABLE 8.3 IMPORTS OF NITROANILINE COMPOUNDS

1974 to 1978 (kkg/year)[1]

Compound	1978	1977	1976[3]	1975[2]	1974
2,4-dinitroaniline	100	170	170	54	270
2-chloro-4-nitroaniline	230	270	180	147	160
2-chloro-5-nitroaniline	--	5	30	2	0.7
4-chloro-2-nitroaniline	--	50	--	--	--
4-chloro-3-nitroaniline	--	1	0.8	2	5
2-bromo-2,6-dinitroaniline	10	--	--	--	40

[1] United States International Trade Commission (1974-1978). Imports of Benzenoid Chemicals and Products. The import figures do not reflect any imports from air transportation. See footnote 3.

Those places in the table where dashes occur indicate that no imports were reported for the compound during that year.

The USITC Imports of Benzenoid Chemicals and Products and tables for 1974, 75, 76, 77, and 78 do not reflect the entire import amount. Each report states a "statistical coverage": the estimated fraction of the total imports that was actually reported. The statistical coverage values used for the compounds in this table were the ones that applied to the category, "intermediates."

Year	Statistical Coverage Value
1978	76 percent
1977	81 percent
1976	80 percent
1975	94 percent
1974	99 percent

Footnotes to Table 8.3 continued.

The values in the table have been corrected for less-than-total reporting using the statistical coverage value. This was attained by applying the following formula to each value in the table:

$$\text{Import Compound at 100\% Value} = \frac{\text{USITC Reported Import Quantity x 100\%}}{\text{USITC Statistical Coverage Value (\%)}}$$

[2] The import figures for 1975 were not readily available and attempts to obtain these figures were unsuccessful.

[3] Personal communications between Ron Burger, JRB Associates, Inc., McLean, Virginia, and Mr. Magnusson, Office of Rubber and Chemicals, U.S. Department of Commerce.

9.0 CHLORO- AND BROMOANILINES

9.1 PHYSICAL PROPERTIES

The physical properties of the chloro- and bromoanilines to be reviewed in this chapter are shown in Table 9.1. Quantitative solubility data were unavailable; qualitative characterizations are presented as a general guideline.

TABLE 9.1 PHYSICAL PROPERTIES OF CHLORO- AND BROMOANILINES[1]

CLASS	COMPOUND	MELTING POINT	BOILING POINT	SOLUBILITY IN H_2O	TEMPERATURE AT V.P. of 1 Torr
Monochloro-anilines	o-chloro	-2.3°	208-210°	insol	46.3°C
	m-chloro	-10.6°	228-231°	insol	63.5°C
	p-chloro-	69.5°	229-233°	sol (hot)	59.3°C
Dichloro-anilines	2,3-dichloro-				
	2,4-dichloro-				
	2,5-dichloro-	47-50°	251-252°	slight	
	3,4-dichloro-	68-72°	272°	slight	
	3,5-dichloro-				
Trichloro-anilines	2,4,6-trichloro	78.5°	262°	insol	134°C
Tetrachloro-anilines	2,3,4,5-tetrachloro-	118-120°			
	2,3,4,6-tetrachloro-				
	2,3,5,6-tetrachloro-	108°		insol	
Pentachloro-anilines	2,3,4,5,6-penta-chloro-	232°			
Monobromo-anilines	p-bromo-	66.4°		insol	
Tribromo-anilines	2,4,6-tribromo-	122°	300°	insol	

[1] Sources: Hawley, 1977; Weast, 1977-78.

9.2 MATERIALS BALANCE FOR CHLORO- AND BROMOANILINES

In view of the lack of information available on the chloro- and bromoanilines of interest, neither individual materials balance diagrams nor a composite diagram was constructed.

9.3 DIRECT PRODUCTION OF CHLORO- AND BROMOANILINES

9.3.1 Production Processes, Producers, and Locations

Figure 9.1 collects the available data on the producers of chloro- and bromoanilines, their locations, and the organic synthetic reactions used.

9.3.2 Amounts Produced

No quantitative data were available on amounts of chloro- or bromoanilines produced. This information may be available from the following sources: 1) Chemical Marketing Reporter or other trade periodicals; 2) By a complete analysis, starting with amounts of end-products (e.g., specific dyes) utilizing a particular haloaniline and working backwards to account for all consumption by either importation or domestic production.

9.3.3 Emissions Due to Direct Production

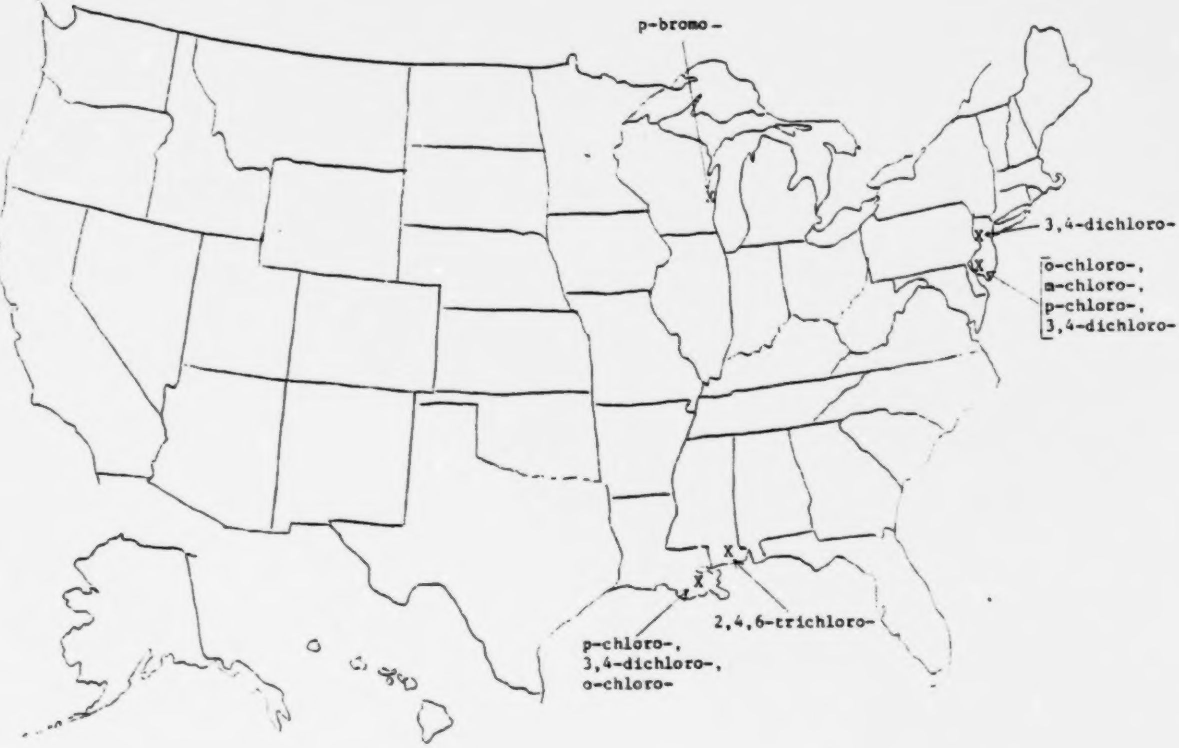
In the absence of production data, it was not possible to calculate useful emissions values due to production.

9.4 INDIRECT PRODUCTION

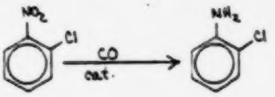
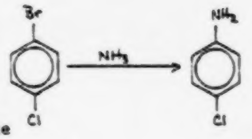
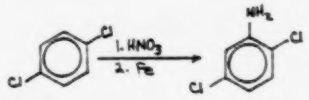
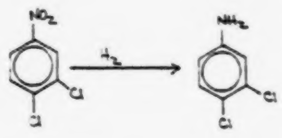
9.4.1 Chlorination of Waste Anilines

Chlorination is sometimes applied to waste stream in order to disinfect. It has long been known that Cl_2 reacts with activated aromatic rings to produce chloroaromatics. The classic example is the chlorination of phenol (Morris, 1975) to produce mono-, di-, and trichlorophenols. It is quite possible that a similar reaction would take place on aniline, which is also quite susceptible to electrophilic attack (note, however, that nitroanilines would be deactivated and would probably not chlorinate). We suggest that this might be a mechanism for production of chloroanilines from aniline in waste streams. The physical result could be settling out of less-soluble chloroanilines. Additional research is needed in this area to evaluate the contribution of this reaction to the overall aniline materials balance, and the relative toxicities of aniline and chloroanilines.

FIGURE 9.1 CHLORO- AND BROMOANILINE PRODUCTION


p-bromo-
3,4-dichloro-
o-chloro-,
m-chloro-,
p-chloro-,
3,4-dichloro-
2,4,6-trichloro-
p-chloro-,
3,4-dichloro-,
o-chloro-

PRODUCERS, LOCATIONS, CHEMISTRY

COMPOUND	SYNTHESIS REACTION	1978	1977	1976	1975	1974
o-chloroaniline	 NO₂ Cl CO cat. NH₂ Cl	duPont Deepwater, NJ Monsanto Luling, LA	Upjohn Co. North Haven CT Bofors Lakeway, Inc. Muskegon, MI (45–450 kkg)	duPont	duPont	duPont Monsanto
m-chloroaniline	n.a.	duPont	Napp Chem. Lodi, NJ (0.5–5 kkg) duPont	duPont	duPont	duPont GAF Corp. Linden, NJ
p-chloroaniline	 Br NH₃ NH₂ Cl Cl	duPont Monsanto	Monsanto (45–450 kkg) duPont	duPont Monsanto	duPont Monsanto	duPont Monsanto
2,5-dichloroaniline	 Cl Cl 1. HNO₃ 2. Fe NH₂ Cl Cl	n.a.	duPont Carroll Prod. Wood Riv. Jct. RI Drake Chem Lock Haven, PA	n.a.	duPont	n.a.
3,4-dichloroaniline	 NO₂ H₂ NH₂ Cl Cl Cl Cl	Blue Spruce Co. Bound Brook NJ duPont Monsanto	Eagle Riv. Chem., W. Helena, AR Monsanto (45–450 kkg) duPont	n.a.	n.a.	n.a.

PRODUCERS, LOCATIONS, CHEMISTRY

COMPOUND	SYNTHESIS REACTION	1978	1977	1976	1975	1974
2,4,6-trichloroaniline	n.a.	Plastifax, Inc. Gulfport, MI	Tennessee Eastman (45-450 kkg) Columbia Org. Chem. ($<$ 0.5 kkg) Upjohn Co. North Haven CT Fike Chemicals Nitro, WV Plastifax, Inc. Carroll Prod. Chem. Systems Div. San Jose, CA (5-450 kkg) Drake Chem.	n.a.	duPont Eagle River Chem. Co. Helena, AR Monsanto	n.a.
p-bromaniline	n.a.	Aldrich Chem. Milwaukee, WI	Eastman Kodak Rochester, NY	Eastman Kodak	Eastman Kodak	Eastman Kodak
2,4,6-tribromoaniline	n.a.	n.a.	Kodak Park Div. Rochester, NY Great Lakes Chem. West Lafayette, IN	n.a.	n.a.	n.a.
2,4-dichloroaniline	n.a.	n.a.	Tennessee Eastmen Kingsport, TN (0.5-5 kkg)	n.a.	n.a.	n.a.
2,3-dichloroaniline	n.a.	n.a.	Monsanto Luling, LA duPont Deepwater, NJ	n.a.	n.a.	n.a.

Source: USITC, 1976-79; Hancock, 1975; U.S. EPA, 1977

9.5 IMPORTS OF CHLORO- AND BROMOANILINES

9.5.1 Amounts

Table 9.2 summarizes the information on imports of chloro- and bromoanilines that was readily available. Emissions due to importation of o-chloroaniline and m-chloroaniline could be estimated by applying the oil spill/risk model described in section 2.3.2.1. The estimated emissions which are obtained by multiplying a small amount of imported anilines x a very small emission factor (7×10^{-9} kkg/kkg transported), would be very small. Useful emissions estimates for the solid chloro- and bromoanilines were not possible.

9.6 CONSUMPTION AND USE

Table 9.3 summarizes qualitative data available on consumption and uses of haloanilines. No quantitative data were available, so no useful estimates of emissions could be made.

TABLE 9.3 CONSUMPTION AND USES OF CHLOROANILINES[1]

COMPOUND	USES
o-chloroaniline	Dye intermediate, colorimetric standard, petroleum solvents, fungicides
m-chloroaniline	Azo dyes and pigments, pharmaceuticals, insecticides, agricultural chemicals
p-chloroaniline	Dye intermeidate, pharmaceuticals, agricultural chemicals
2,5-dichloroaniline	Dye intermediate
3,4-dichloroaniline	Dye intermediate, biologically active compounds

[1] Source: Hawley, 1977.

TABLE 9.2 IMPORTS OF CHLORO- AND BROMOANILINE COMPOUNDS

1974-1978 (kkg/year)[1]

Compound	1978	1977	1976	1975[2]	1974
o-chloroaniline	240	210	1990	63	40
m-chloroaniline	40	120	60	2	1
p-chloroaniline	50	60	40	33	110
2,3-dichloroaniline	10	4	.6	.03	--
2,4-dichloroaniline	--	--	10	--	--
2,5-dichloroaniline	190	150	10	56	--
2,4,6-trichloroaniline	5	.06	--	--	100
p-bromoaniline	.1	--	--	--	--

[1] United States International Trade Commission (1974-1978). Imports of Benzenoid Chemicals and Products. The import figures do not reflect any imports from air transportation. See footnote 3.

Those places in the table where dashes occur indicate that no imports were reported for the compound during that year.

The USITC Imports of Benzenoid Chemicals and Products and tables for 1974, 75, 76, 77, and 78 do not reflect the entire import amount. Each report states a "statistical coverage": the estimated fraction of the total imports that was actually reported. The statistical coverage values used for the compounds in this table were the ones that applied to the category, "intermediates."

Year	Statistical Coverage Value
1978	76 percent
1977	81 percent
1976	80 percent
1975	94 percent
1974	99 percent

The values in the table have been corrected for less-than-total reporting using the statistical coverage value. This was attained by applying the following formula to each value in the table:

$$\text{Import Compound at 100\% Value} = \frac{\text{USITC Reported Import Quantity} \times 100\%}{\text{USITC Statistical Coverage Value (\%)}}$$

Footnotes for Table 9.2 continued

[2] The import figures for 1975 were not readily available and attempts to obtain these figures were unsuccessful.

[3] Personal communications between Ron Burger, JRB Associates, Inc., McLean, Virginia, and Mr. Magnusson, Office of Rubber and Chemicals, U.S. Department of Commerce.

10. LOCATIONS OF EMISSIONS

This chapter will collect the information already presented on locations of producers of anilines in order to identify sites with a large point source or multiple sources. The results are shown in table form (Table 10.1).

The table shows that the only locations with multiple compounds produced were Bound Brook, NJ (two producers making three products); Deepwater, NJ (one producer making three products); and Sauget, IL (one producer making two products). Bound Brook, NJ, is the only city with two separate producers (American Cyanamid and Blue Spruce Co.). It is important to note, however, that this analysis will not be complete until consumption sites - the major points of estimated emissions - can be tabulated and analyzed in the same way.

TABLE 10.1 LOCATIONS OF EMISSIONS

Location	Anilines							
	Aniline	Aniline HCl	Aniline HBr	o-nitro-	m-nitro-	p-nitro	Other nitro	Chloro- & bromo-
Bound Brook, NJ	X	X						X
Deepwater, NJ				X		X		X
Gibbstown, NJ	X							
Linden, NJ								X
Toms River, NJ							X	
Coventry, RI							X	
North Haven, CT							X	
Renssalaer, NY							X	
Rochester, NY								X
Huntington, WV							X	
New Martinsville, WV	X							
Willow Island, WV	X							
Lock Haven, PA						X		
Sodyeco, NC							X	
Bushy Park, SC							X	
Gulfport, MS								X
Pascagoula, MS	X							
Geismar, LA	X							
Luling, LA								X
Shreveport, LA						X		
Beaumont, TX	X							
Helena, AR								X
Kingsport, TN		X						
Charles City, IA							X	
Milwaukee, WI								X
Sauget, IL				X		X		

11.0 DATA GAPS

During the preparation of this report, a series of significant data gaps were identified. Several of these have been mentioned in earlier chapters, and they will be summarized here.

11.1 PRODUCERS AND AMOUNTS PRODUCED FOR LESS-WIDELY-PRODUCED ANILINES

It was not possible to calculate emissions due to production for the compounds aniline hydrochloride, m-nitroaniline, and the grouped nitroanilines and haloanilines because of the absence of production data. Since the actual production figures are proprietary, an estimate based on another approach (like plant capacity analysis or back-calculation starting with consumption data) might be needed.

11.2 CONSUMPTION AND USE INFORMATION FOR LESS-WIDELY-USED ANILINES

Consumption data are necessary to the estimation of emissions due to consumption. These data were lacking for the compounds aniline hydrochloride, m-nitroaniline, and the grouped nitroanilines and haloanilines. It might be possible to obtain this information from a plant-by-plant analysis of 1) products marketed, 2) chemistry of a particular product's synthesis, and 3) how much of the product was made per year. This might be feasible in a Level II or Level III materials balance. Another important question about consumption is: how much of the input aniline was carried over into the product? Chemical analyses of products would be necessary to answer the question.

11.3 DATA ON EFFLUENT ANALYSIS OR EMISSION FACTORS FOR ANILINE PRODUCTION

Because the estimation of emissions to water during aniline production is a key value to obtain, it should be calculated at least two ways. More data are needed concerning waste stream analyses and waste treatment procedures, preferably on a plant-by-plant basis.

11.4 ACCESS TO IMPORT AND EXPORT DATA WITHIN THE 'BASKET' CATEGORIES

Information on relevant imports and exports are sometimes available but hidden within the USITC's "all other" category. It would be helpful if there were a procedure for obtaining information from these "basket" categories on short notice.

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APPENDIX A

Description of Aniline Production by Catalytic Vapor-Phase Hydrogenation of Nitrobenzene

Source: Lowenheim, F. A., and Moran, M. K. (eds), 1975. Faith, Keyes, and Clark's Industrial Chemicals, 4th ed. c 1975 by John Wiley and Sons, Inc. Reprinted by permission.

Nitrobenzine containing less than 10 ppm thiophene is vaporized in a stream of hydrogen and passed into a reactor containing a fluidized bed of copper catalyst. The catalyst is made by spray-drying a silica hydrogel upon which cuprammonium nitrate has been adsorbed. The catalytic powder (10 to 20% copper) (20 to 150 m) is activated in place in the reactor by treatment with hydrogen at 250°C. The nitrobenzene vapor-hydrogen mixture (300% excess hydrogen) is fed through a porous distributor plate in the bottom of the fluidized bed reactor held at 270°C and 5 psi (34.5 kPa). Excess heat of reaction is removed by circulating a cool heat-transfer fluid through tubes suspended in the catalyst bed. Exit gasses are filtered free of catalyst fines on porous stainless-steel filters in the top of the reactor.

The filtered product gasses are condensed, further cooled, and sent to a liquid separator or decanter. Excess hydrogen is recycled. The lower layer of liquid in the separator (crude aniline containing less than 0.5% nitrobenzene and 5% water) is distilled to remove high boilers. The water and aniline vapors that pass overhead are separated by further distillation.

The upper (aniline water) layer from the separator is pumped to an extraction column, where it passes countercurrent to cold nitrobenzene for recovery of dissolved aniline. A yield of 98% is claimed for the process.

The catalyst will produce 1500 kg aniline/kg of catalyst before regeneration is required. Regeneration is accomplished in place by flushing the system with an inert gas, and then passing air through the catalyst at 250 to 350°C to burn off organic deposits.

Several different catalysts have been patented for use in aniline processes similar to that described. Operating procedures will of course vary with the activity and ruggedness of the catalyst used. An effective catalyst for a fixed-bed hydrogenation is nickel sulfide deposited on alumina.

APPENDIX B PRODUCTS DERIVED FROM ANILINE[1]

PRODUCTION PROCESS	DERIVATIVE	USES
Aniline + acetic anhydride or aniline + glacial acetic acid (27)	ACETANILIDE (27)	Manufacture of p-nitroaniline and o-nitroaniline (27) Sulphonamide Intermediate (27) Hydrogen Peroxide Stabilizer Cellulose Ester Lacquers Manufacture of Dyes and Intermediates Analgesic and Antipyretic Manufacture (36) Sulfa Drugs (33) Local Anesthetic (33)
Aniline + ethylacetoacetate Aniline + diketene (36)	ACETOACETANILIDE (27)	Dye Intermediate Manufacture of Benzidine Yellow Pigments (27)
Aniline + phosgene vapor or organic solvents (27)	PHENYL ISOCYANATES (27)	Manufacture of Isocyanates urethanes disubstituted ureas Insecticides and Herbicides (27)
Methanol + aniline + sulphuric acid under heat and pressure (27) Aniline + formaldehyde reduced by zinc and sodium hydroxide (27)	N-METHYLANILINE N,N-METHYLANILINE (27)	p-dimethylaminobenzaldehyde manufacture (27)
Aniline + excess methanol + acid catalyst under heat and pressure (27)	N,N-DIMETHYLANILINE (27)	Dye Intermediate (33)

APPENDIX B PRODUCTS DERIVED FROM ANILINE[1]

PRODUCTION PROCESS	DERIVATIVE	USES
Aniline + hydrochloride + ethanol under heat and pressure (27)	N-ETHYLANILINE (27)	Manufacture of Stabilizer For Explosives (27) Vulcanization Accelerator (36)
Aniline + sulphuric acid (27)	SULPHANILIC ACID (27)	Manufacture of Three Sulphonilic Acids Intermediate in Azo Dyestuffs and a Component in 91 Dyes (27)
Aniline + carbon disulphide + sulphur heated in an autoclave (27)	2-MERCAPTOBENZOTHIZOLES (27)	Manufacture of Vulcanization Accelerators (27) Sulphonamide Vulcanization Accelerators (27)
Aniline + aldehydes + organic acid as a catalyst (27)	ALDEHYDE-AMINE REACTION PRODUCTS (27)	Manufacture of Vulcanization Accelerators (27)
Cyanogen chloride + hot aqueous aniline (27)	1,3-DIPHENYLGUANIDINE (27)	Manufacture of Vulcanization Accelerators (27)
Aniline + carbon disulphite (27)	THIOCARBANILIDE (27)	Accelerator for Specific Rubbers (27)
Aniline + hydrochloric acid as a catalyst or substituted aniline with ketones + hydrochloric acid (27)	2,2,4-TRIMETHYL-1,2-DIHYDROQUINOLINE (27)	Rubber Antioxidant (27)
Condensation of hydroquinone and two moles of aniline + acid catalyst (27)	N,N-DIPHENYL-P-PHENYLENEDIAMINE (27)	Rubber Chemicals antiozonant (28) antioxidant (28)

APPENDIX B PRODUCTS DERIVED FROM ANILINE[1]

PRODUCTION PROCESS	DERIVATIVE	USES
Liquid phase catalytic hydrogenation of aniline under pressure at 135°-170°C and under 50 - 500 atmospheres in the presence of a catalyst (27) (31)	CYCLOHEXYLAMINE (27)	Major Use: Manufacture of Sodium and Calcium Cyclohexyl-Sulphamates used in the Manufacture of Synthetic Sweetening Agents (27) Derivatives Used in the Manufacture: Rubber Chemicals: vulcanization accelerators antioxidants antiozonants Corrosion Inhibitors - ferric metals Plastic Resins Intermediate in Dyestuffs (27) Used Directly in Boiler Water Limit Scaling and Corrosion Dyestuff Intermediates (27)
Vapor phase reaction with nickel catalyst of aniline	DICYCLOHEXYLAMINE (27)	Corrosion Inhibitors Ferrous Metal Articles Derivatives: Form Sulphonamides Used as Rubber Accelerators Salts and Metal Compounds Used in Textile, Paint and Varnish Industry (27)
Aniline is oxidized by manganese dioxide or sodium dichromate in sulfuric acid to quinone. Quinone is reduced by iron in water (31)	HYDROQUIONONE (31)	Photographic Developer (28) Polymerization Inhibitors in Monomers (28) Manufactures of BHA Food Antioxidant (28)

APPENDIX B PRODUCTS DERIVED FROM ANILINE[1]

PRODUCTION PROCESS	DERIVATIVE	USES
	ANILINE (REFER TO FOOTNOTE 2)	Rubber Chemicals: acceleratorss (36) antioxidants (28) antidegradant (33) curing agents (33) elastomers (33) MDI Production (33) Dyes: Intermediate: (39) stilbene triarylmethane azine dyes indigoid dyes Dyes (33) Predye Fiber Treatment (33)(34) Catalysts: (33) polymerization reactions organic reactions organometallic reactions metallurgical industry Patina production Resins: (33) production of epoxy resins and harding agents production plastics (38) aniline formaldehyde resins (33) Petroleum: (33) antiknock - gasoline knock suppressor-aviation fuel

APPENDIX B PRODUCTS DERIVED FROM ANILINE[1]

PRODUCTION PROCESS	DERIVATIVE	USES
	ANILINE (continued)	Rocket Fuels: (33) ignition fuels self-flammable fuel mixture Explosives: (38) detonator constituent for gunpowder Agriculture Uses: (33) intermediate for pest sprays Reagents: (33) qualitative detection of metals papermaking process Electronic Industry: (33) polishing diode and transistors Solvent for Organic Reactions (33)

1. The table presents ANILINE and its Derivatives, their method of production and uses as gleaned from readily available references. The reference list that applies to this appendix only is attached.

2. The referenced resources stated uses for "aniline and derivatives" but did not state the aniline compound nor the production process. Therefore, uses stated under aniline may be from derivatives of aniline rather than aniline directly.

APPENDIX B PRODUCTS DERIVED FROM ANILINE HYDROCHLORIDE

PRODUCTION PROCESS	DERIVATIVE	USES
Heating aniline and aniline hydrochloride at 210°-240°C at 90 psi in the absence of a catalyst, 30 to 35 hours (33)	DIPHENYLAMINE (1, 28, 31, 33)	Rubber Industry antioxidants (28) antiozonants (27) retarder (28) stabilizer (36) Agriculture antihelminthics (28) insecticides (31) fungicide (33) Dye Industry preparation of azo dyes (31) printing (1, 30) dyestuff intermediate (36) Miscellaneous stabilizer for explosives (28, 36) metallurgy - plating baths (33) organic synthesis[1]
Heating aniline hydrochloride with ethanol at 180°C, refluxing with ethanol over Raney (33)	N-ETHYLANILINE (33)	Rocket Fuel (33) Dye Intermediate (31)
Heating aniline hydrochloride with excess ethanol at 180°C under pressure (31)	DIETHYLANILINE (31)	Herbicide (10)
Aniline hydrochloride plus excess bromide (27)	2,4,6-TRIBROMOANILINE (27)	

[1] The category "organic synethesis" refers to the use of diphenylamine in the synthesis of numerous organic compounds.

APPENDIX B PRODUCTS DERIVED FROM ortho-NITROANILINE

PRODUCTION PROCESS	DERIVATIVE	USES
Reduction of o-nitroaniline with sodium sulphide under pressure (28, 36)	o-PHENYLENEDIAMINE (27, 36)	Antioxidants inhibitor of copper corrosion (27) antifreeze preparations (27) lubricating oils (27) polishes detergents (27) Rubber Chemicals and Intermediates (27) Dyes C.I. Oxidation Base 16 (27) hair dyes (36) optical bleaches (27) dyestuff intermediate (27) Pharmaceutical Products (27) Veterinary Products antihelminthics (27) Miscellaneous redox indicator (27) chemical detection of metals (27)
	o-NITROANILINE	Dyes preparation of azo and anthraquinone dyes (1, 3, 27) azoic diazo component 6 (27) Photographic Antifogging Agents (1, 36) Coccidostatis (1) Interior Paint Pigments (1)
	N-CYCLOALKENIC (27)	Insecticides and Intermediates (27)

APPENDIX B PRODUCTS DERIVED FROM meta-NITROANILINE

PRODUCTION PROCESS	DERIVATIVE	USES
Reduction of m-nitroaniline with iron and dilute acid or catalytic hydrogenation (31)	m-TOLUIDINE (31)	Dye Preparation (31)
	m-NITROANILINE (27)	Organic Synthesis (3, 31) Dye Intermediate (3, 27, 31, 36) Synthetic Sweeteners (31, 33)

APPENDIX B PRODUCTS DERIVED FROM para-NITROANILINE

PRODUCTION PROCESS	DERIVATIVE	USES
Reduction of p-nitroaniline by iron or sulfide (27)	N-SUBSTITUTED p-PHENYLENEDIAMINES	Antioxidants and Antiozonants (27, 28, 31) Hair and Fur Dye, Azo, Azine, Sulfur, and Cyanine Dyestuffs (27) Dye Intermediate (27)
Reduction of p-nitroaniline with iron and dilute acid or catalytic hydrogenation (31)	p-TOLUIDINE (31)	Dye Production (31) Organic Synthesis (31)
Diazotization of p-nitroaniline with HCl and sodium nitrite (31)	p-NITROANILINE HYDROCHLORIDE (31)	Dyes (31)
Nitration of p-nitroaniline (27)	2,4,6-TRINITROANILINE (PICRAMIDE) (27)	
Direct chlorination of p-nitroaniline in benzene solution at 20°C with tert-butyl hypochlorite (33)	2,6-DICHLORO-4-NITROANILINE (33)	
	p-NITROANILINE	Corrosion Inhibitor (1) Veterinary and Pharmaceutical Products (1, 3) Agricultural Chemicals (3) Dyes and Dye Intermediates (1, 31) Gasoline Additives (1, 3) Rubber Chemicals antioxidants (1) Fungicides Botran (28)

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